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On the Use of the Energy-Momentum Principle in General Relativity – RICHARD C. TOLMAN 875
On the Use of the Entropy Principle in General Relativity – – – – RICHARD C. TOLMAN 886
On the Weight of Heat and Thermal Equilibrium in General Relativity – RICHARD C. TOLMAN 904
Determination of Electron Distributions from Measurements of Scattered X-Rays – – – – ARTHUR H. COMPTON 925
Two Notes on the Probability of Radiative Transitions – – – – – J. R. OPPENHEIMER 939
Boundary Conditions and the Meaning of Wave Groups in Wave Mechanics – H. A. WILSON 948
Heat of Dissociation of Carbon Monoxide – – – – – – – – – JOSEPH KAPLAN 957
Band Spectrum of Silver Chloride – – – – – – – – – BROOKS A. BRICE 960
Relation between the Intensity and Position of the Overtones of Some Organic Liquids – – – – P. E. SHEARIN 973
Magnetic Susceptibility of Rubidium – – – – – – – – – – – C. T. LANE 977
Secondary Electrons from Contaminated Surfaces – – – – – – PAUL L. COPELAND 982
Thomson Effect in Zinc Crystals – – – – – – – – – – – – L. A. WARE 989
E. M. F., Resistance, and Capacitance Phenomena in Photovoltaic Cells Containing Grignard Reagents – – – – – – – – – – – – – H. E. HAMMOND 996
Thermal Convection – – – – – – – – – – – – – R. W. BABCOCK 1008
Letters to the Editor – – – – – – – – – – – – – – – – 1014
Book Reviews – – – – – – – – – – – – – – – – – 1017

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As a summary the abstract should give briefly the conclusions of the article important advances in experimental technique and theory, and all numerical results of general interest that may be conveniently given including all that might belong in a hand book and table of contents. It should give all the information that readers who are not specialists in the particular field involved might desire to know about the article thus saving them the time and trouble in referring to the article itself. Experience has shown that in general the length of the abstract should be from four to eight percent of the length of the article.

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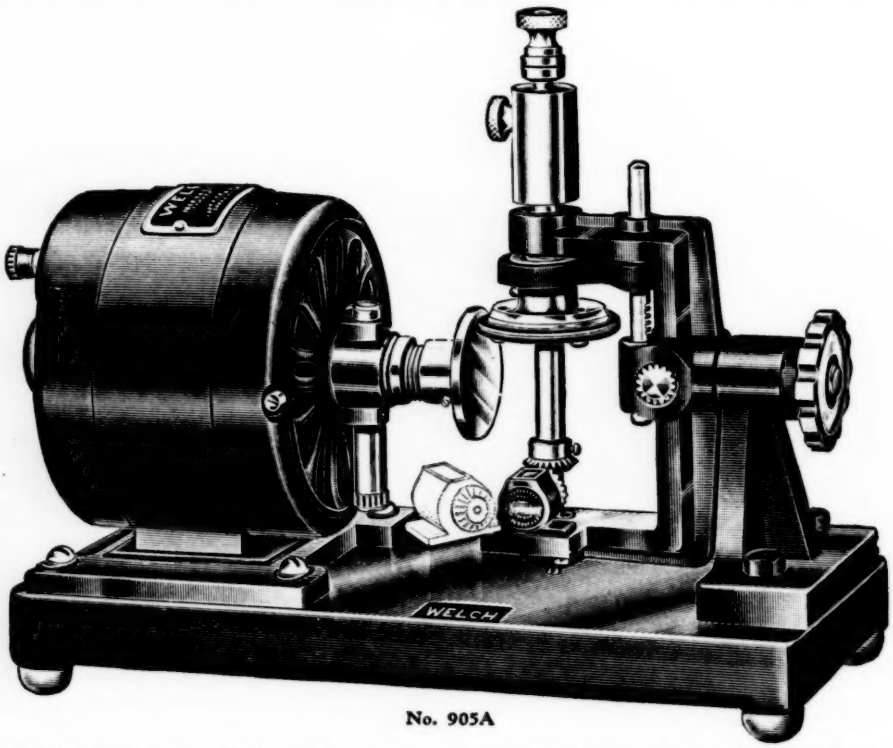

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PHYSICAL REVIEW

ON THE USE OF THE ENERGY-MOMENTUM PRINCIPLE IN GENERAL RELATIVITY

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(Received December 20, 1930)

Abstract

The primary purpose of this article is to obtain from the general relativity form of the energy-momentum principle certain new consequences which are needed for later work that the author has in mind. In addition, it is the intention to give at the same time a somewhat comprehensive and coherent treatment of the principle and its consequences, which it is hoped will increase the confidence and facility of physicists in the use of this important part of the general theory of relativity. In carrying out the investigation, it has seemed desirable for English readers, to take Eddington's "Mathematical Theory of Relativity" as a starting point, and this has incidentally led to a new form of deduction for certain consequences of the energy-momentum principle that were already known.

After presenting the energy-momentum principle in the form discovered by Einstein and showing its application to the case of the conservation of energy in an isolated system, an important expression is derived which gives the total densities of energy and momentum in the form of a divergence. This expression is equivalent to one previously obtained by Einstein but on account of the starting point adopted is derived and expressed in terms of the quantities $\mathfrak{g}^{\mu\nu}$ and $\mathfrak{g}_{\alpha}^{\mu\nu}$ instead of the $g^{\mu\nu}$ and $g_{\alpha}^{\mu\nu}$. Following this, the limiting values at large distances from an isolated material system are obtained for the quantities $\mathfrak{g}^{\alpha\beta}\partial\mathfrak{R}/\partial\mathfrak{g}_{\gamma}^{\alpha\beta}$ and $\mathfrak{g}^{\alpha_4}\partial\mathfrak{R}/\partial\mathfrak{g}_{\gamma}^{\alpha_4}$. These values, which have considerable use, have not previously received explicit expression. This is followed by a deduction from our present starting point of Einstein's famous relation $U=m$ between the energy and gravitational producing mass of an isolated system. An important expression is then obtained which gives the energy of a quasi-static isolated system in the form of an integral which has to be extended only over the portion of space actually occupied by matter or radiation. This expression has not previously received a satisfactory derivation. The result is used to obtain an expression for the energy of a spherical distribution of a perfect fluid, and it is then shown that this expression, in the case of a sphere of ordinary material, approaches in a sufficiently weak field to the classical expression for energy including the potential gravitational energy. This result is not only intrinsically useful, but also shows for a particular case that a higher order of approximation to the general relativity value for total energy is obtained by including the classical gravitational energy than by going at once to flat space-time as is often done. Finally, a general consideration is given to the problem of determining the conditions imposed on those changes from one static state to another which could occur in a non-isolated system forming part

of a larger static system, without changing the distribution of matter and radiation outside the boundary and without contravening the energy-momentum principle as applied to the system as a whole.

§1. Introduction

IN ACCORDANCE with Einstein's development of the general theory of relativity, the relativity analogues of the classical principles of the conservation of energy and momentum are to be obtained with the help of integration from the well-known differential equation[1]

$$\frac{\partial}{\partial x_\nu}(\mathfrak{T}_\mu^\nu + \mathfrak{t}_\mu^\nu) = 0 \tag{1}$$

where $\mathfrak{T}_\mu^\nu$ is the tensor density of material energy and momentum and $\mathfrak{t}_\mu^\nu$ is the psuedo-tensor density of potential gravitational energy and momentum. Considering x_4 to be the time-like coordinate, equation (1) leads to the three equations for the conservation of momentum with $\mu = 1, 2, 3$, and leads to the equation for the conservation of energy with $\mu = 4$.

Taking for illustration the latter case, multiplying the equation by $dx_1\, dx_2\, dx_3$, and integrating over the system of interest, we obtain with some rearrangement of terms

$$\frac{\partial}{\partial x_4}\iiint (\mathfrak{T}_4^4+\mathfrak{t}_4^4)dx_1dx_2dx_3$$

$$= -\iiint\left[\frac{\partial}{\partial x_1}(\mathfrak{T}_4^1+\mathfrak{t}_4^1)+\frac{\partial}{\partial x_2}(\mathfrak{T}_4^2+\mathfrak{t}_4^2)+\frac{\partial}{\partial x_3}(\mathfrak{T}_4^3+\mathfrak{t}_4^3)\right]dx_1dx_2dx_3$$

and by performing the indicated integrations on the right hand side this can be rewritten in the form

$$\frac{\partial}{\partial x_4}\iiint (\mathfrak{T}_4^4+\mathfrak{t}_4^4)dx_1dx_2dx_3$$

$$= -\iint\left|\mathfrak{T}_4^1+\mathfrak{t}_4^1\right|_{x_1}^{x_1'}dx_2dx_3 - \iint\left|\mathfrak{T}_4^2+\mathfrak{t}_4^2\right|_{x_2}^{x_2'}dx_1dx_3 - \iint\left|\mathfrak{T}_4^3+\mathfrak{t}_4^3\right|_{x_3}^{x_3'}dx_1dx_2 \tag{2}$$

where the limits of integration are denoted by x_1, x'_1 etc. The result states that the rate of change with the time (x_4) in the value of the integral on the left hand side of the equation can be calculated from the conditions prevailing at the boundary of the system of interest as given by the right hand side of the equation. The equation can thus be regarded as a statement of the energy principle provided we define the energy of the system by the expression

$$U = \iiint (\mathfrak{T}_4^4+\mathfrak{t}_4^4)dx_1dx_2dx_3. \tag{3}$$

And a similar treatment for the components of momentum can be obtained by taking $\mu = 1, 2, 3$.

[1] See for example Eddington, "The Mathematical Theory of Relativity." Cambridge 1923, equations (59.2) and (59.3).

Owing to the fact that equations (1) and (2) are not tensor equations and that the quantity t_μ^ν is not a true tensor density, considerable doubt as to the validity of the above formulation of the energy principle was at one time expressed[2] and perhaps to some extent still exists.[3] It can be shown, nevertheless, that the equations have the necessary fundamental property of being true in all sets of coordinates, and a completely satisfactory justification of the formulation was finally given by Einstein in 1918.[4]

Since that time, however, the interest of mathematical physicists has been largely turned to other matters, and the methods and results of applying the energy-momentum principle have not been particularly investigated. It is the purpose of the present article to consider some of these methods and results not only because of their intrinsic importance, but also because of certain further applications which the writer has in mind.

In carrying out the investigation we shall use, as far as may be, the notation adopted by Eddington in his "Mathematical Theory of Relativity", and shall base our deductions on equations given by him. This choice of starting point necessitates some duplication of results which have previously been obtained by other methods, but seems desirable owing to the familiarity of English readers with Eddington's treatise and owing to the excellence of the detailed and coherent treatment which he has given.

In the immediately following section, §2, we shall first give Einstein's method of applying the above energy principle to an isolated material system. In §3 we shall then obtain a very useful formula which expresses the total density of energy and momentum as an ordinary divergence; the formula is equivalent in import to one already obtained by Einstein but because of our choice of starting point differs in method of derivation and form of expression. Following this, in §4, we shall deduce the limiting values at large distances from such an isolated system of certain functions of the gravitational field; these values are necessary for our further work and have not previously received explicit expression. In §5 we shall then be able to give a deduction from our present basis of Einstein's relation between the total energy and gravitational mass of an isolated material system. In §6 we shall deduce an extremely important equation expressing the total energy of an isolated system by an integral which has to be extended only over that portion of space which is actually occupied by matter or radiation; this equation

[2] Schroedinger, Phys. Zeits. **19**, 4 (1918); Bauer, ibid. **19**, 163 (1918).

[3] Thus, for example, Eddington (reference 1, pp. 135–136) objects to the fundamental significance of the equation $\partial/\partial x_\nu(\mathfrak{T}_\mu^\nu+t_\mu^\nu)=0$ on the ground that t_μ^ν is not a true tensor density, and appears to regard the introduction of the equation as an unfortunate pandering to an immoral desire to obtain by hook or crook some kind of conservation laws in the mechanics of general relativity. It should be remarked, however, that the appropriate criterion for the fundamental significance of equations should not be that they are written in tensorial form but that they are written in covariant form so as to be true in all sets of coordinates. All tensor equations are indeed covariant equations, but this does not exclude the possibility of covariant equations, such as the one above, which are not tensorial. To assume the contrary would be the fallacy of the Dormouse in Alice in Wonderland, who said:—"I breathe when I sleep" is the same thing as "I sleep when I breathe."

[4] Einstein, Berl. Ber. 1918, p. 448.

has not previously received a satisfactory derivation. In the following section, §7, we shall use this equation to obtain an expression for the total energy of a distribution of perfect fluid having spherical symmetry. And in §8 we shall show that, on making the gravitational field weaker, the above expression approaches the classical expression for the energy of such a sphere including the classical value for its potential gravitational energy; the result is an intrinsically useful one and also shows for a particular case that a higher order of approximation to the general relativity value for total energy is obtained by including the classical gravitational energy than by neglecting the gravitational energy entirely as has hitherto often been done. Finally in §§9, 10 we shall consider the application of the general energy-momentum principle to changes occurring within a region which forms part of a larger system, and in §11 shall make some concluding remarks.

§2. The Conservation of Energy in an Isolated System

Let us now first consider the application of the energy principle to those changes which can take place within a limited system without producing any changes in the gravitational field outside of a sufficiently distant boundary located in the free space surrounding the system. Such a system will be called an isolated one. In this case, we can easily show that the general energy principle, as given by equation (2), can be interpreted as leading to the conservation of energy within the boundary taken.

For the tensor density of matter and energy $\mathfrak{T}_\mu^\nu$, occurring in equation (2), we can write from the equation of definition[5]

$$\mathfrak{T}_\mu^\nu = \sqrt{-g}\, g_{\alpha\mu} T^{\alpha\nu} = \sqrt{-g}\, g_{\alpha\mu} \rho_0 \frac{dx_\alpha}{ds} \frac{dx_\nu}{ds} \tag{4}$$

where ρ_0 is the proper density of matter. And since we take the boundary which encloses the system as located in free space the density ρ_0 will there be zero, so that it is evident that the quantities $\mathfrak{T}_4^1$, $\mathfrak{T}_4^2$ and $\mathfrak{T}_4^3$, occurring on the right hand side of equation (2), will themselves have the value zero at the boundary.

Furthermore, the pseudo-tensor density of potential energy is defined in terms of the Lagrangian function $\mathfrak{L}$ and the cosmological constant Λ by the equation[6]

$$\mathfrak{t}_\mu^\nu = \frac{1}{16\pi}\left\{ g_\mu^\nu \mathfrak{L} - \mathfrak{g}_\mu^{\alpha\beta} \frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_\nu^{\alpha\beta}} \right\} + \frac{\Lambda}{8\pi} g_\mu^\nu \sqrt{-g}. \tag{5}$$

The quantity g_μ^ν, however, is equal to zero with $\mu \neq \nu$, and the symbol $\mathfrak{g}_4^{\alpha\beta}$ is a short hand for $\partial(g^{\alpha\beta}\sqrt{-g})/\partial x_4$ and hence is equal to zero at the boundary enclosing our system, if the gravitational field at that boundary is not changing with the time as postulated. Hence the quantities $\mathfrak{t}_4^1$, $\mathfrak{t}_4^2$, and $\mathfrak{t}_4^3$,

[5] See Eddington, reference 1, equation (53.1).

[6] See Eddington, reference 1, equation (59.4). The additional term in Λ, when the cosmological term is not neglected, can easily be shown necessary. Compare Einstein, reference 4, equation (18).

occurring on the right hand side of equation (2), will also be zero at the boundary with which we have enclosed the system.

Hence using a system of coordinates such that the limits of integration coincide with the boundary enclosing the system,[7] it is evident that the terms on the right hand side of equation (2) will all of them become zero and the energy principle for this particular case will reduce to the conservation of energy

$$\frac{\partial}{\partial x_4}\int\int\int (\mathfrak{T}_4^4+\mathfrak{t}_4^4)dx_1dx_2dx_3=0$$

or

$$U=\int\int\int (\mathfrak{T}_4^4+\mathfrak{t}_4^4)dx_1dx_2dx_3=\text{const.} \tag{6}$$

§3. The Densities of Momentum and Energy Expressed as Divergences

In order to make use of this interesting result, it will now be necessary to make a rather lengthy digression by deducing certain useful lemmas in this and in the following section. In the present section we shall show the possibility of expressing the total density of momentum or energy as an ordinary divergence in accordance with the equation[8]

$$8\pi(\mathfrak{T}_\mu^\nu+\mathfrak{t}_\mu^\nu)=\frac{\partial}{\partial x_\gamma}\left(-\mathfrak{g}^{\alpha\nu}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\gamma^{\mu\alpha}}+\frac{1}{2}g_\mu^\nu\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\gamma^{\alpha\beta}}\right). \tag{7}$$

To prove this equation will be a very tiresome business, justified only by the importance of the result. To carry out the demonstration we shall have to make use of a large number of well established results which we shall now give.

For the density of material energy and momentum we shall use the fundamental equation connecting it with the metrical properties of the field[9]

$$-8\pi\mathfrak{T}_\mu^\nu=\mathfrak{G}_\mu^\nu-\tfrac{1}{2}g_\mu^\nu\mathfrak{G}+\Lambda\mathfrak{g}_\mu^\nu \tag{8}$$

where $\mathfrak{G}_\mu^\nu$ is the tensor density corresponding to the contracted Riemann-Christoffel tensor and Λ the cosomological constant. For the density of potential energy and momentum we shall use the equation of definition already given above

$$16\pi\mathfrak{g}_\mu^\nu=g_\mu^\nu\mathfrak{L}-\mathfrak{g}_\mu^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\nu^{\alpha\beta}}+2\Lambda\mathfrak{g}_\mu^\nu \tag{9}$$

[7] With a system of coordinates chosen so that some of the limits of integration do not fall on the boundary, the quantities $|\mathfrak{T}_4^1+\mathfrak{t}_4^1|x_1'$ etc. will not necessarily be zero. Compare §9.

[8] This equation is equivalent in import to equation (18) given by Einstein, Berl. Ber. 1916, p. 1115. It differs in form since we are regarding $\mathfrak{L}$ as a function of the $\mathfrak{g}^{\mu\nu}$ and $\mathfrak{g}_\alpha^{\mu\nu}$ instead of as a function of the $g^{\mu\nu}$ and $g_\alpha^{\mu\nu}$.

[9] See Eddington, reference 1, equation (54.71).

where the Lagrangian function $\mathfrak{L}$ is defined in terms of the Christoffel symbols by the equation[10]

$$\mathfrak{L}=\sqrt{-g}\,g^{\alpha\beta}\Big(\{\alpha\gamma,\epsilon\}\{\beta\epsilon,\gamma\}-\{\alpha\beta,\gamma\}\{\gamma\epsilon,\epsilon\}\Big). \tag{10}$$

In accordance with this definition it is possible to show that $\mathfrak{L}$ can also be expressed as a function of the quantities

$$\mathfrak{g}^{\alpha\beta}=g^{\alpha\beta}\sqrt{-g} \quad \text{and} \quad \mathfrak{g}^{\alpha\beta}_{\gamma}=\frac{\partial}{\partial x_\gamma}(g^{\alpha\beta}\sqrt{-g}) \tag{11}$$

and will then have the differential coefficients[11]

$$\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\alpha\beta}}=-\Big(\{\alpha\gamma,\epsilon\}\{\beta\epsilon,\gamma\}-\{\alpha\beta,\gamma\}\{\gamma\epsilon,\epsilon\}\Big) \tag{12}$$

and[12]

$$\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\alpha\beta}_{\gamma}}=-\{\alpha\beta,\gamma\}+\frac{1}{2}g^{\gamma}_{\alpha}\{\beta\epsilon,\epsilon\}+\frac{1}{2}g^{\gamma}_{\beta}\{\alpha\epsilon,\epsilon\}. \tag{13}$$

Further important properties of the Lagrangian function, relating it to the metrical properties of the field, are given by the equation[13]

$$G_{\mu\nu}=\frac{\partial}{\partial x_\gamma}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\mu\nu}_{\gamma}}-\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\mu\nu}} \tag{14}$$

and[14]

$$\mathfrak{H}=\frac{\partial}{\partial x_\gamma}\Big(\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\alpha\beta}_{\gamma}}\Big)-\mathfrak{L}. \tag{15}$$

Finally, the quantity $\mathfrak{g}^{\alpha\beta}_{\gamma}$ may be expressed in terms of the Christoffel symbols by the equation[15]

$$\mathfrak{g}^{\alpha\beta}_{\gamma}=\sqrt{-g}\Big(-\{\delta\gamma,\alpha\}g^{\delta\beta}-\{\delta\gamma,\beta\}g^{\delta\alpha}+\{\gamma\delta,\delta\}g^{\alpha\beta}\Big). \tag{16}$$

We are now ready to proceed to the derivation of equation (7). Combining equations (8) and (9) we have

$$8\pi(\mathfrak{T}^{\nu}_{\mu}+\mathfrak{t}^{\nu}_{\mu})=-\mathfrak{H}^{\nu}_{\mu}+\frac{1}{2}g^{\nu}_{\mu}\mathfrak{H}+\frac{1}{2}g^{\nu}_{\mu}\mathfrak{L}-\frac{1}{2}\mathfrak{g}^{\alpha\beta}_{\mu}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\alpha\beta}_{\nu}}$$

[10] See Eddington, reference 1, equation (58.1).

[11] See Eddington, reference 1, equation (58.51).

[12] See Eddington, reference 1, equation (58.52). We have written the expression in a symmetrical form which is equivalent to Eddington's unsymmetrical form.

[13] See Eddington, reference 1, equation (58.6).

[14] See Eddington, reference 1, equation (58.8).

[15] See Eddington, reference 1, the equation immediately following (58.72).

Substituting (14) and (15) we obtain

$$8\pi(\mathfrak{T}_\mu^\nu+\mathfrak{t}_\mu^\nu)=-\mathfrak{g}^{\alpha\nu}\frac{\partial}{\partial x_\gamma}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\gamma^{\mu\alpha}}+\mathfrak{g}^{\alpha\nu}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\mu\alpha}}+\frac{1}{2}g_\mu^\nu\frac{\partial}{\partial x_\gamma}\left(\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\gamma^{\alpha\beta}}\right)-\frac{1}{2}\mathfrak{g}_\mu^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\nu^{\alpha\beta}}$$

and this can evidently be rewritten in the form

$$8\pi(\mathfrak{T}_\mu^\nu+\mathfrak{t}_\mu^\nu)=\frac{\partial}{\partial x_\gamma}\left(-\mathfrak{g}^{\alpha\nu}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\gamma^{\mu\alpha}}+\frac{1}{2}g_\mu^\nu\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\gamma^{\alpha\beta}}\right)+\mathfrak{g}_\gamma^{\alpha\nu}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\gamma^{\mu\alpha}}+\mathfrak{g}^{\alpha\nu}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\mu\alpha}}-\frac{1}{2}\mathfrak{g}_\mu^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\nu^{\alpha\beta}}. \quad (17)$$

Comparing this result with equation (7), we see that our deduction will be completed if we can now show that the sum of the last three terms is equal to zero. To accomplish this we must substitute for the quantities occurring in these three terms their explicit values in terms of the Christoffel symbols as given by equations (12), (13) and (16). Doing so we obtain

$$\begin{aligned}
&\mathfrak{g}_\gamma^{\alpha\nu}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_\gamma^{\mu\alpha}}+\mathfrak{g}^{\alpha\nu}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\mu\alpha}}-\frac{1}{2}\mathfrak{g}_\mu^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}^{\alpha\beta}}\\
&=\sqrt{-g}\left[-\left\{\delta\gamma,\alpha\right\}g^{\delta\nu}-\left\{\delta\gamma,\nu\right\}g^{\delta\alpha}+\left\{\gamma\delta,\delta\right\}g^{\alpha\nu}\right]\left[-\left\{\mu\alpha,\gamma\right\}+\tfrac{1}{2}g_\mu^\gamma\left\{\alpha\epsilon,\epsilon\right\}+\tfrac{1}{2}g_\alpha^\gamma\left\{\mu\epsilon,\epsilon\right\}\right]\\
&\quad+\sqrt{-g}\,g^{\alpha\nu}\left[-\left\{\alpha\gamma,\epsilon\right\}\left\{\mu\epsilon,\gamma\right\}+\left\{\alpha\mu,\gamma\right\}\left\{\gamma\epsilon,\epsilon\right\}\right]\\
&\quad-\tfrac{1}{2}\sqrt{-g}\left[-\left\{\delta\mu,\alpha\right\}g^{\delta\beta}-\left\{\delta\mu,\beta\right\}g^{\delta\alpha}+\left\{\mu\delta,\delta\right\}g^{\alpha\beta}\right]\left[-\left\{\alpha\beta,\nu\right\}+\tfrac{1}{2}g_\alpha^\nu\left\{\beta\epsilon,\epsilon\right\}\right.\\
&\quad\left.+\tfrac{1}{2}g_\beta^\nu\left\{\alpha\epsilon,\epsilon\right\}\right]\\
&=\sqrt{-g}\left[\overset{(1)}{\left\{\delta\gamma,\alpha\right\}}\left\{\mu\alpha,\gamma\right\}g^{\delta\nu}-\tfrac{1}{2}\overset{(2)}{\left\{\delta\mu,\alpha\right\}}\left\{\alpha\epsilon,\epsilon\right\}g^{\delta\nu}-\tfrac{1}{2}\overset{(3)}{\left\{\delta\alpha,\alpha\right\}}\left\{\mu\epsilon,\epsilon\right\}g^{\delta\nu}\right.\\
&\qquad+\overset{(4)}{\left\{\delta\gamma,\nu\right\}}\left\{\mu\alpha,\gamma\right\}g^{\delta\alpha}-\tfrac{1}{2}\overset{(5)}{\left\{\delta\mu,\nu\right\}}\left\{\alpha\epsilon,\epsilon\right\}g^{\delta\alpha}-\tfrac{1}{2}\overset{(6)}{\left\{\delta\alpha,\nu\right\}}\left\{\mu\epsilon,\epsilon\right\}g^{\delta\alpha}\\
&\qquad-\overset{(7)}{\left\{\gamma\delta,\delta\right\}}\left\{\mu\alpha,\gamma\right\}g^{\alpha\nu}+\tfrac{1}{2}\overset{(8)}{\left\{\mu\delta,\delta\right\}}\left\{\alpha\epsilon,\epsilon\right\}g^{\alpha\nu}+\tfrac{1}{2}\overset{(3)}{\left\{\alpha\delta,\delta\right\}}\left\{\mu\epsilon,\epsilon\right\}g^{\alpha\nu}\\
&\qquad-\overset{(1)}{\left\{\alpha\gamma,\epsilon\right\}}\left\{\mu\epsilon,\gamma\right\}g^{\alpha\nu}+\overset{(7)}{\left\{\alpha\mu,\gamma\right\}}\left\{\gamma\epsilon,\epsilon\right\}g^{\alpha\nu}\\
&\qquad-\tfrac{1}{2}\overset{(4)}{\left\{\delta\mu,\alpha\right\}}\left\{\alpha\beta,\nu\right\}g^{\delta\beta}+\tfrac{1}{4}\overset{(5)}{\left\{\delta\mu,\nu\right\}}\left\{\beta\epsilon,\epsilon\right\}g^{\delta\beta}+\tfrac{1}{4}\overset{(2)}{\left\{\delta\mu,\alpha\right\}}\left\{\alpha\epsilon,\epsilon\right\}g^{\delta\nu}\\
&\qquad-\tfrac{1}{2}\overset{(4)}{\left\{\delta\mu,\beta\right\}}\left\{\alpha\beta,\nu\right\}g^{\delta\alpha}+\tfrac{1}{4}\overset{(2)}{\left\{\delta\mu,\beta\right\}}\left\{\beta\epsilon,\epsilon\right\}g^{\delta\nu}+\tfrac{1}{4}\overset{(5)}{\left\{\delta\mu,\nu\right\}}\left\{\alpha\epsilon,\epsilon\right\}g^{\beta\alpha}\\
&\qquad\left.+\tfrac{1}{2}\overset{(6)}{\left\{\mu\delta,\delta\right\}}\left\{\alpha\beta,\nu\right\}g^{\alpha\beta}-\tfrac{1}{4}\overset{(8)}{\left\{\mu\delta,\delta\right\}}\left\{\beta\epsilon,\epsilon\right\}g^{\beta\nu}-\tfrac{1}{4}\overset{(8)}{\left\{\mu\delta,\delta\right\}}\left\{\alpha\epsilon,\epsilon\right\}g^{\alpha\nu}\right]\\
&\qquad=0
\end{aligned}$$

where the value zero arises, after some changes in dummy suffixes, from the mutual cancellation of all terms, as can easily be verified by noting that the terms have been labelled in such a way that those which destroy each other are given the same number.

Combining this result with equation (17), we now complete the derivation of the original equation (7), which it was the purpose of this section to prove.

§4. The Limiting Values of Certain Quantities at Large Distances from an Isolated Material System

As a further preparation for our later considerations we shall now obtain the limiting values at large distances from an isolated material system for the quantities $\mathfrak{g}^{\alpha\beta}(\partial\mathfrak{L}/\partial\mathfrak{g}_\gamma^{\alpha\beta})$ and $\mathfrak{g}^{\alpha 4}(\partial\mathfrak{L}/\partial\mathfrak{g}_\gamma^{\alpha 4})$ which occur on the right hand side of equation (7). To do this we recall that we have defined an isolated system in §2, in such a way that the changes taking place within the system do not produce changes in the gravitational field outside of a sufficiently distant boundary. Therefore, at a sufficient distance from an isolated system the gravitational field will be static and spherically symmetrical, and we can use for it the well known Schwarzschild solution. Hence placing the system in the neighborhood of the origin of a set of coordinates x, y, z, t, which approach Galilean coordinates at large distances we can write for the line element the approximate Schwarzschild expression[16]

$$ds^2=-(1+2m/r)(dx^2+dy^2+dz^2)+(1-2m/r)dt^2$$

where the constant m is the mass of the system and r is an abbreciation for $(x^2+y^2+z^2)^{1/2}$.

Since the above expression gives the form taken by the Schwarzschild solution in a particular kind of quasi-Galilean coordinates, it is evident that later results, which are dependent on the present section, will also be originally derived in the form which they assume in these particular coordinates, and their translation into the language of other systems of coordinates must be undertaken with due cognizance of their method of derivation. Furthermore, the above expression is an approximate one, valid at distances large enough so that terms of the order $(m/r)^2$ can be neglected, and yet at the same time small enough so that the curvature of the universe as a whole, as given by the cosmological term, can be neglected. Hence those later considerations which are dependent on this section will primarily apply only to systems which are small compared to the total dimensions of the universe, even though of course still very large compared with ordinary terrestrial dimensions.

Returning to our approximate expression for the Schwarzschild line element we may now write for the components of the fundamental metrical tensor, the values

$$\begin{aligned}
&g_{11}=g_{22}=g_{33}=-[1+2m/r] && g_{44}=[1-2m/r] \\
&g^{11}=g^{22}=g^{33}=-\frac{1}{[1+2m/r]} && g^{44}=\frac{1}{[1-2m/r]} \\
&g_{\mu\nu}=g^{\mu\nu}=0 \qquad (\mu\neq\nu) && \sqrt{-g}=[1+2m/r]^{3/2}[1-2m/r]^{1/2}
\end{aligned} \tag{18}$$

To calculate the desired quantities from these expressions for the metrical tensor, we shall first need the values of the Christoffel symbols. These are defined by the equation [17]

[16] See Eddington, reference 1, equation (46.15).

[17] See Eddington, reference 1, equation (27.2).

$$\{\mu\nu,\sigma\} = \frac{1}{2}\, g^{\sigma\lambda}\left(\frac{\partial g_{\mu\lambda}}{\partial x_\nu} + \frac{\partial g_{\nu\lambda}}{\partial x_\mu} - \frac{\partial g_{\mu\nu}}{\partial x_\lambda}\right)$$

which evidently reduces under our circimstances to

$$\{\mu\nu,\sigma\} = \frac{1}{2}\, g^{\sigma\sigma}\left(\frac{\partial g_{\mu\sigma}}{\partial x_\nu} + \frac{\partial g_{\nu\sigma}}{\partial x_\mu} - \frac{\partial g_{\mu\nu}}{\partial x_\sigma}\right) \qquad \text{(not summed)}$$

and taking μ, ν, and σ as *different* indices we obtain the four cases

$$\begin{aligned}
\{\mu\mu,\mu\} &= \frac{1}{2}\, g^{\mu\mu}\frac{\partial g_{\mu\mu}}{\partial x_\mu} \\
\{\mu\mu,\nu\} &= -\frac{1}{2}\, g^{\nu\nu}\frac{\partial g_{\mu\mu}}{\partial x_\nu} \\
\{\nu\mu,\mu\} &= \{\mu\nu,\mu\} = \frac{1}{2}\, g^{\mu\mu}\frac{\partial g_{\mu\mu}}{\partial x_\nu} \\
\{\mu\nu,\sigma\} &= 0.
\end{aligned} \tag{19}$$

We are now ready to proceed to our calculations. Under our circumstances we may evidently write

$$\mathfrak{g}^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \underset{1}{\mathfrak{g}}^{\alpha\beta}} = \sqrt{-g}\left(g^{11}\frac{\partial \mathfrak{L}}{\partial \underset{1}{\mathfrak{g}}^{11}} + g^{22}\frac{\partial \mathfrak{L}}{\partial \underset{1}{\mathfrak{g}}^{22}} + g^{33}\frac{\partial \mathfrak{L}}{\partial \underset{1}{\mathfrak{g}}^{33}} + g^{44}\frac{\partial \mathfrak{L}}{\partial \underset{1}{\mathfrak{g}}^{44}}\right).$$

Substituting the values given by equation (13), this becomes

$$\begin{aligned}
\mathfrak{g}^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \underset{1}{\mathfrak{g}}^{\alpha\beta}} = \sqrt{-g}\Big(&-g^{11}\{11,1\} + \frac{1}{2}g^{11}\{1\epsilon,\epsilon\} + \frac{1}{2}g^{11}\{1\epsilon,\epsilon\} \\
&- g^{22}\{22,1\} - g^{33}\{33,1\} - g^{44}\{44,1\}\Big)
\end{aligned}$$

and introducing the values of the Christoffel symbols given by equations(19) it reduces to

$$\begin{aligned}
\mathfrak{g}^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \underset{1}{\mathfrak{g}}^{\alpha\beta}} = \frac{1}{2}\sqrt{-g}\Big(&g^{11}g^{22}\frac{\partial g_{22}}{\partial x} + g^{11}g^{33}\frac{\partial g_{33}}{\partial x} + g^{11}g^{44}\frac{\partial g_{44}}{\partial x} \\
&+ g^{22}g^{11}\frac{\partial g_{22}}{\partial x} + g^{33}g^{11}\frac{\partial g_{33}}{\partial x} + g^{44}g^{11}\frac{\partial g_{44}}{\partial x}\Big).
\end{aligned}$$

Finally, substituting the values for the components of the metrical tensor given by equations (18), and, because of the large distances under consideration, neglecting quantities of the order m/r in comparison with unity, we easily obtain

$$\mathfrak{g}^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_1{}^{\alpha\beta}} = -2\frac{\partial}{\partial x}\left(\frac{2m}{r}\right) + \frac{\partial}{\partial x}\left(\frac{2m}{r}\right) = \frac{2m}{r^2}\,\frac{\partial r}{\partial x}.$$

From considerations of symmetry it is evident that we shall also have similar expressions in y and z, and introducing the direction cosines for the radius vector we may evidently write

$$\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha\beta}_{1}}=\frac{2m}{r^2}\cos(nx),\quad \mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha\beta}_{2}}=\frac{2m}{r^2}\cos(ny),\quad \mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha\beta}_{3}}=\frac{2m}{r^2}\cos(nz)\quad(20)$$

while the value of the fourth quantity $\mathfrak{g}^{\alpha\beta}(\partial\mathfrak{Y}/\partial\mathfrak{g}^{\alpha\beta}_{4})$ will not be needed for our later work.

Turning now to the second of the quantities of interest mentioned at the beginning of this section, we may evidently write with the help of equations (18), (13) and (19)

$$\mathfrak{g}^{\alpha 4}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha 4}_{1}}=\sqrt{-g}\,g^{44}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{44}_{1}}=-\sqrt{-g}\,g^{44}\left\{44,1\right\}=\frac{1}{2}\sqrt{-g}\,g^{44}g^{11}\frac{\partial g_{44}}{\partial x}$$

or, to the same order of approximation as before, we obtain

$$\mathfrak{g}^{\alpha 4}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha 4}_{1}}=-\frac{m}{r^2}\cos(nx),\quad \mathfrak{g}^{\alpha 4}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha 4}_{2}}=-\frac{m}{r^2}\cos(ny),\quad \mathfrak{g}^{\alpha 4}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha 4}_{3}}=-\frac{m}{r^2}\cos(nz).\quad(21)$$

§5. Relation Between the Energy and Mass of an Isolated System

We are now ready to return to our discussion of the energy principle by giving a deduction from our present basis of Einstein's relation between the energy and mass of an isolated material system. Using the quasi-Galilean coordinates described in the last section, we may write for the energy of the system, in accordance with equation (6),

$$U=\iiint(\mathfrak{T}^4_4+\mathfrak{t}^4_4)\,dx\,dy\,dz$$

and this quantity will be constant independent of the time t as shown in §2, provided the boundary of the region of integration is taken sufficiently distant from the system. Substituting the value for total energy density given by equation (7), we can now rewrite our expression for the energy in the form

$$U=\frac{1}{8\pi}\iiint\frac{\partial}{\partial x_\gamma}\left(-\mathfrak{g}^{\alpha 4}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha 4}_{\gamma}}+\frac{1}{2}\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha\beta}_{\gamma}}\right)dx\,dy\,dz.$$

Taking the boundary of the region of integration as a sphere with its center at the origin of coordinates, using Gauss's theorem to transform to a surface integral, and substituting at the distant boundary the three values for the term in parenthesis found in the previous section as given by equations (20) and (21), this can evidently be rewritten in the form

$$U=\frac{1}{8\pi}\iint\frac{2m}{r^2}\left[\cos^2(nx)+\cos^2(ny)+\cos^2(nz)\right]dS$$
$$+\frac{1}{8\pi}\frac{\partial}{\partial t}\iiint\left(-\mathfrak{g}^{\alpha 4}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha 4}_{4}}+\frac{1}{2}\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{Y}}{\partial\mathfrak{g}^{\alpha\beta}_{4}}\right)dx\,dy\,dz.$$

Since, however, both U and the surface integral on the right hand side of the equation are constants independent of the time,[18] it is evident that the second term on the right hand side of the equation must be zero, as the volume integral in the second term could not continue to change permanently at a constant rate with the time. Hence evaluating the surface integral, we easily obtain for an isolated system the simple relation

$$U = m \tag{22}$$

where U is Einstein's expression for the energy of the system, and m is the mass which must be substituted into the Schwarzschild solution to give the gravitational field at large distances. This appropriate result is itself no mean justification for Einstein's formulation of the energy principle.

§6. The Energy of a Quasi-static Isolated System Expressed by an Integral Extending Only Over the Occupied Space

For certain purposes both of the expressions for the energy of an isolated system, $\iiint(\mathfrak{T}_4^4+\mathfrak{t}_4^4)dxdydz$ and m, are somtimes unsatisfactory, the first because the integration has to be extended over a region large compared with the actual system, owing to the fact that $\mathfrak{t}_4^4$ is in general not zero in free space, and the second because it gives no method of computing the energy from the actual distribution of matter or radiation within the system. For a particular class of systems, which we shall call quasistatic, a more usable expression can be obtained.

Starting once more with our fundamental equation (6) for the energy of an isolated system, we write

$$U = \iiint (\mathfrak{T}_4^4+\mathfrak{t}_4^4)dxdydz$$

where we again use the quasi-Galilean coordinates defined in §4. Substituting the expression for the density of potential energy $\mathfrak{t}_4^4$ given by equation (9) this can be rewritten in the form[19]

$$U = \iiint \left(\mathfrak{T}_4^4+\frac{\mathfrak{P}}{16\pi}-\frac{1}{16\pi}\mathfrak{g}_4^{\alpha\beta}\frac{\partial\mathfrak{P}}{\partial\mathfrak{g}_4^{\alpha\beta}}\right)dxdydz$$

and introducing the expression for $\mathfrak{P}$ given by equation (15) this becomes

$$U = \iiint \left[\mathfrak{T}_4^4-\frac{\mathfrak{H}}{16\pi}+\frac{1}{16\pi}\frac{\partial}{\partial x_\gamma}\left(\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{P}}{\partial\mathfrak{g}_\gamma^{\alpha\beta}}\right)-\frac{1}{16\pi}\mathfrak{g}_4^{\alpha\beta}\frac{\partial\mathfrak{P}}{\partial\mathfrak{g}_4^{\alpha\beta}}\right]dxdydz.$$

[18] The quantity m must be a constant, since it determines the gravitational field at the distante boundary, and by our definition an isolated system produces a constant gravitational field at the distant boundary.

[19] We omit the cosmological term in the expressions for $\mathfrak{t}_4^4$ and $\mathfrak{T}$ since our present considerations already contain the assumption that the system is small compared with the total dimensions of the universe.

Substituting now for $\mathfrak{G}$ the well-known expression[19]

$$\mathfrak{G}=8\pi\mathfrak{T}=8\pi(\mathfrak{T}_1^1+\mathfrak{T}_2^2+\mathfrak{T}_3^3+\mathfrak{T}_4^4)$$

writing the third term of the integrand out in full, and combining with the last term, we then easily obtain

$$U=\frac{1}{2}\int\int\int(\mathfrak{T}_4^4-\mathfrak{T}_1^1-\mathfrak{T}_2^2-\mathfrak{T}_3^3)dxdydz$$

$$+\frac{1}{16\pi}\int\int\int\left[\frac{\partial}{\partial x}\left(\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_1^{\alpha\beta}}\right)+\frac{\partial}{\partial y}\left(\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_2^{\alpha\beta}}\right)+\frac{\partial}{\partial z}\left(\mathfrak{g}^{\alpha\beta}\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_3^{\alpha\beta}}\right)\right]dxdydz \qquad (23)$$

$$+\frac{1}{16\pi}\int\int\int\mathfrak{g}^{\alpha\beta}\frac{\partial}{\partial t}\left(\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_4^{\alpha\beta}}\right)dxdydz.$$

The second integral on the right hand side of this equation can be evaluated, however, by taking the boundary of the region of integration as a sphere, transforming to a surface integral and substituting at the distant boundary the values given by equations (20). We thus easily obtain $m/2$ as the value of the second integral and since for an isolated system this is itself equal by equation (22) to $U/2$ as shown in the preceding section, we can rewrite equation (23) in the form

$$U=\int\int\int(\mathfrak{T}_4^4-\mathfrak{T}_1^1-\mathfrak{T}_2^2-\mathfrak{T}_3^3)dxdydz+\frac{1}{8\pi}\int\int\int\mathfrak{g}^{\alpha\beta}\frac{\partial}{\partial t}\left(\frac{\partial\mathfrak{L}}{\partial\mathfrak{g}_4^{\alpha\beta}}\right)dxdydz \qquad (24)$$

Finally, let us now define a quasi-static system as one in which changes with the time are taking place sufficiently slowly so that the last term in this equation can be neglected in comparison with the others, as will of course be exactly true in case we are only interested in the energy of the system at times when it is in a quiescent state of temporary or permanent equilibrium. We can then write as the desired expression[20] for the energy of an isolated quasi-static system

$$U=\int\int\int(\mathfrak{T}_4^4-\mathfrak{T}_1^1-\mathfrak{T}_2^2-\mathfrak{T}_3^3)dxdydz \qquad (25)$$

[20] This expression for energy was first given by Nordström, Proc. Amster. Acad. **202,** 1080 (1918). The derivation given for the expression, however, was unsatisfactory since it was made to depend on an equation which the author ascribed to von Laue without any citation of the place of publication nor statement as to its range of validity. I have myself not been able to find the source of this expression and Professor von Laue has informed me by letter that he has been unable to find such an expression in the second volume of his book on relativity, does not know how he could have arrived at such an equation, now where else he might have set it forth, and is inclined to believe that Nordström must have been in error concerning the reference. Attention should also be called in this connection to the limited range as to the nature of the system and the choice of coordinates which will make equation (25) valid.

where it is evident from the equation of definition

$$T^{\mu\nu} = \rho_0 \frac{dx_\mu}{ds} \frac{dx_\nu}{ds}$$

that the integration has to be extended only over the region actually occupied by matter or radiation.

§7. Energy of a Sphere of Perfect Fluid.

We may now use equation (25) to calculate the energy of a spherical distribution of perfect fluid in a static state of stable or metastable equilibrium.

Continuing to use our quasi-Galilean coordinates x, y, z, t, we may evidently write the line element for our spherically symmetrical and static system in the form

$$ds^2 = -e^\mu (dx^2+dy^2+dz^2) + e^\nu dt^2 \tag{26}$$

where μ and ν are functions of $r=(x^2+y^2+z^2)^{1/2}$ and independent of t. In accordance with this line element we have for the components of the fundamental metrical tensor

$$\begin{aligned} &g_{11}=g_{22}=g_{33}=-e^\mu && g_{44}=e^\nu \\ &g^{11}=g^{22}=g^{33}=-e^{-\mu} && g^{44}=e^{-\nu} \\ &g_{\rho\sigma}=g^{\rho\sigma}=0 \quad (\rho\neq\sigma) && \sqrt{-g}=e^{\frac{3\mu+\nu}{2}}. \end{aligned} \tag{27}$$

For the tensor of energy and momentum for a perfect fluid we have the well known equation[21]

$$T^{\rho\sigma} = (\rho_{00}+p_0)\frac{dx_\rho}{ds}\frac{dx_\sigma}{ds} - g^{\rho\sigma}p_0 \tag{28}$$

where ρ_{00} and p_0 are the proper *macroscopic* density and proper pressure of the fluid as measured by local observers, and the quantities (dx_ρ/ds) are *macroscopic* velocities. For our case the macroscopic velocities will all be zero except for the case $\rho=\sigma=4$ and we shall then have

$$\left(\frac{dt}{ds}\right)^2 = g^{44} = e^{-\nu}$$

so that the surviving components of the energy tensor will be

$$T^{11} = T^{22} = T^{33} = e^{-\mu}p_0 \qquad T^{44} = e^{-\nu}\rho_{00}$$

or lowering suffixes

$$T^1_1 = T^2_2 = T^3_3 = -p_0 \qquad T^4_4 = \rho_{00} \tag{29}$$

Multiplying these results by $\sqrt{-g}$ to change to tensor densities and substituting in equation (25), we now obtain for the energy of a steady spherical distribution of perfect fluid

[21] See Eddington, reference 1, equations (54.81) and (54.82).

$$U = \iiint (\rho_{00}+3p_0)e^{\frac{3\mu+\nu}{2}}dxdydz. \tag{30}$$

We also have, moreover, the general relation

$$dV_0 ds = \sqrt{-g}dx_1dx_2dx_3dx_4$$

where dV_0 is the element of proper three dimensional volume, and in our case this reduces to

$$dV_0 = e^{\frac{3\mu+\nu}{2}}dxdydz\frac{dt}{ds} = e^{3\mu/2}dxdydz$$

so that equation (30) can be rewritten in the extremely simple form

$$U = \int(\rho_{00}+3p_0)\, e^{\nu/2}\, dV_0 = \int(\rho_{00}+3p_0)\sqrt{g_{44}}dV_0. \tag{31}$$

§8. Approximate Expression for the Energy of a Sphere of Fluid in a Weak Gravitational Field

We shall now investigate the value of this expression, for the energy of a sphere of perfect fluid, under circumstances where the gravitational field is weak enough so that the Newtonian theory of gravitation is approximately valid. Such a condition can of course be achieved by taking the quantity of matter in the sphere sufficiently small.

Under these circumstances the line element will approach that for flat space-time and we may write the components of the metrical tensor in the form

$$g_{\mu\nu} = \delta_{\mu\nu} + h_{\mu\nu} \tag{32}$$

where the quantities $\delta_{\mu\nu}$ are the Galilean values for the components of the metrical tensor, ± 1 or 0, and the quantities $h_{\mu\nu}$ are *small* deviations therefrom. With these values for the components of the metrical tensor, however, we may easily obtain a well-known relation between h_{44} and the Newtonian gravitational potential Ψ.

To do this let us consider the behavior of a test particle placed at the point of interest and then allowed to move freely under the action of the gravitational field. In accordance with the theory of relativity the motion of this free particle must correspond to a geodesic in space-time and hence be governed by the equation[23]

$$\frac{d^2x_\alpha}{ds^2} + \{\mu\nu,\alpha\}\frac{dx\mu}{ds}\frac{dx_\nu}{ds} = 0. \tag{33}$$

Since the particle starts from rest, however, the initial "velocities" dx_μ/ds and dx_ν/ds will all be zero except with μ or $\nu = 4$, and taking first the case of $\alpha = 1$, the above equation will reduce at the beginning of the motion to

[22] See Eddington, reference 1, equation (49.42).

[23] See Eddington, reference 1, equation (28.5).

$$\frac{d^2x}{ds^2} + \{44,1\}\left(\frac{dt}{ds}\right)^2 = 0. \tag{34}$$

Furthermore, we have for a particle at rest

$$\begin{aligned} ds^2 &= g_{44}dt^2 = (1 + h_{44})dt^2 \\ &\approx dt^2 \end{aligned} \tag{35}$$

and in general

$$\{44,1\} = \frac{1}{2}g^{\lambda 1}\left(\frac{\partial g_{4\lambda}}{\partial x_4} + \frac{\partial g_{4\lambda}}{\partial x_4} - \frac{\partial g_{44}}{\partial x_\lambda}\right)$$

which for our case reduces with sufficient approximation to

$$\{44,1\} = \frac{1}{2}\frac{\partial g_{44}}{\partial x} = \frac{\partial}{\partial x}\left(\frac{h_{44}}{2}\right). \tag{36}$$

So that substituting (35) and (36) in (34) and writing the analogous equations with $\alpha = 2$ and 3, we easily obtain for the initial acceleration of the test particle the equations

$$\frac{d^2x}{dt^2} = -\frac{\partial}{\partial x}\left(\frac{h_{44}}{2}\right), \qquad \frac{d^2y}{dt^2} = -\frac{\partial}{\partial y}\left(\frac{h_{44}}{2}\right), \qquad \frac{d^2z}{dt^2} = -\frac{\partial}{\partial z}\left(\frac{h_{44}}{2}\right). \tag{37}$$

We note at once that $(h_{44}/2)$ satisfies the same differential equations of motion as the gravitational potential Ψ in the ordinary Newtonian theory, and since h_{44} tends to zero at large distances may now write

$$\frac{h_{44}}{2} = \Psi \tag{38}$$

provided we make the usual convention that the gravitational potential shall be zero at infinity. This equation connects the relativity and Newtonian methods of treatment, providing the gravitational field is weak enough to permit the use of the older method.

In addition to this equation, we shall also need to use a value for a certain integral which was known in the Newtonian theory but is sufficiently unfamiliar so that we shall now derive it. The integral in question is $3\int p dV$, where p is the pressure within the fluid and the integration is to be taken over the volume V of the whole sphere. We write

$$3\int p dV = 3\int_0^R 4\pi r^2 p\, dr$$

where R is the radius of the sphere, and by partial integration obtain

$$\begin{aligned} 3\int p dV &= 4\pi r^3 p\Big|_0^R - \int_0^R 4\pi r^3 dp \\ &= -\int_0^R 4\pi r^3\, dp \end{aligned}$$

where the first term has been dropped since r is zero at one limit and p at the other. It is evident, however, that the quantity $-4\pi r^2 dp$ is the total radial force acting outwards on the spherical shell of material dM_r lying between the radii r and $r+dr$ and hence can be equated to the gravitational attraction acting on this shell which gives us

$$3\int pdV = \int_0^R \frac{M_r}{r} dM_r.$$

Moreover, the quantity on the right hand side of this equation is obviously the work that would be necessary to remove the material of the sphere to infinity and hence the negative of its potential energy. So that we can finally write

$$3\int pdV = -\int \frac{\rho\Psi}{2} dV \tag{39}$$

where the integral on the right hand side of the equation is a well-known expression for potential energy, ρ being the density of material and Ψ the gravitational potential.

We are now ready to return to equation (31) which gave as an exact expression for the total energy of the sphere

$$U = \int (\rho_{00}+3p_0)\sqrt{g_{44}}\, dV_0.$$

In accordance with equations (32) and (38) we can write as approximately valid in the case of a weak field

$$\sqrt{g_{44}} = (1+h_{44})^{1/2} \approx 1 + \frac{h_{44}}{2} = 1+\Psi.$$

And this can be substituted above to give

$$U = \int \rho_{00} dV_0 + \int \rho_{00}\Psi dV_0 + 3\int p_0 dV_0 + 3\int p_0\Psi dV_0.$$

In the case of a weak gravitational field, however, the potential Ψ is everywhere small compared with unity and for the case of ordinary matter in a weak gravitational field[24] p_0 is small compared with ρ_{00}. Hence the last term in the above expression may be dropped entirely and the next two preceding terms simplified by omitting the subscripts $(_0)$ which specify a proper system of coordinates for the measuring of quantities. The result then becomes

$$U = \int \rho_{00} dV_0 + \int \rho\Psi dV + 3\int pdV$$

[24] This is not true for radiation where $p_0 = \rho_{00}/3$, so that our present considerations apply to a sphere in which the density of ordinary matter is large compared with that of radiation, which is of course the case for which the Newtonian potential energy was known.

and introducing the value of $3\int p dV$ given by equation (39), we finally obtain as an approximate expression for the energy of a sphere of perfect fluid in a weak gravitational field

$$U = \int \rho_{00} dV_0 + \int \frac{\rho\Psi}{2} dV. \tag{40}$$

In satisfactory agreement with older theory, the energy thus consists of two parts,—the first being the total proper energy of the material out of which the sphere is composed, and the second the well-known Newtonian expression for its potential gravitational energy.

As far as the writer is aware, this is the first case in which it has been shown that Einstein's exact relativity expression for the energy of a system is more closely approximated by including the Newtonian potential energy than by going at once to flat space-time. It is hoped that the reasonableness of this result will lead to increased confidence in the use of the energy momentum principle in general relativity.

§9. The Interpretation and Use of the Energy-Momentum Principle in the Case of Non-Isolated Systems

So far, the applications of the energy-momentum principle, which we have considered in the foregoing, have dealt with the conservation of energy for an isolated system enclosed within a distant boundary located in the free space surrounding the system, and these applications have been made largely in order to illustrate the reasonableness of Einstein's formulation of the principle. In applying the theory of relativity to the phenomena of nature, however we may often be interested in using the energy-momentum principle to give us information as to the changes which could take place within a limited region which forms part of a larger system. Hence in the present section we shall consider the interpretation and use of the energy-momentum principle when applied to such non-isolated systems, and in the following section we shall discuss specifically the changes which the energy-momentum principle would allow in the distribution of matter within a certain kind of non-isolated system.

Let us return to the fundamental differential equation, true in all sets of coordinates, which was given in §1

$$\frac{\partial}{\partial x_\nu}(\mathfrak{T}_\mu^\nu + \mathfrak{t}_\mu^\nu) = 0 \tag{41}$$

where $\mathfrak{T}_\mu^\nu$ is the tensor density of material energy and momentum and $\mathfrak{t}_\mu^\nu$ the pseudo-tensor density of potential gravitational energy and momentum. Taking x_4 to be the time like coordinate, this equation will lead to the momentum principles with $\mu = 1, 2, 3$ and to the energy principle with $\mu = 4$. For our present purposes, however, we shall leave μ unspecified since the following considerations are general enough to apply to the energy-momentum principle as a whole.

Multiplying the above equation by $dx_1dx_2dx_3$, and integrating over the system of interest we obtain with some rearrangement of terms

$$\frac{\partial}{\partial x_4}\iiint (\mathfrak{T}_\mu^4+\mathfrak{t}_\mu^4)dx_1dx_2dx_3$$
$$=-\iiint\left[\frac{\partial}{\partial x_1}(\mathfrak{T}_\mu^1+\mathfrak{t}_\mu^1)+\frac{\partial}{\partial x_2}(\mathfrak{T}_\mu^2+\mathfrak{t}_\mu^2)+\frac{\partial}{\partial x_3}(\mathfrak{T}_\mu^3+\mathfrak{t}_\mu^2)\right]dx_1dx_2dx_3$$

and, by performing the indicated integrations on the right hand side, this can be rewritten in the form

$$\frac{\partial}{\partial x_4}\iiint (\mathfrak{T}_\mu^4+\mathfrak{t}_\mu^4)dx_1dx_2dx_3$$
$$=-\iint\left|\mathfrak{T}_\mu^1+\mathfrak{t}_\mu^1\right|_{x_1}^{x_1'}dx_2dx_3-\iint\left|\mathfrak{T}_\mu^2+\mathfrak{t}_\mu^2\right|_{x_2}^{x_2'}dx_1dx_3-\iint\left|\mathfrak{T}_\mu^3+\mathfrak{t}_\mu^3\right|_{x_3}^{x_3'}dx_1dx_2 \tag{42}$$

where the limits of integration for the spatial variables x_1, x_2, x_3 are to be chosen so as to include the system of interest.

Equation (42) as written is true in all sets of coordinates, owing to its immediate dependence on the covariant equation (41). The interpretation and use of the equation, however, are often simplified if we choose coordinates in such a way that the limits of integration which must be taken in order to include the system of interest actually lie on the boundary surface which separates the region in question from its surroundings. Thus for example quasi-Galilean coordinates x, y, z with the limits of integration x to x', y to y', and z to z' lying on the boundary of the system, are usually preferable for our present purposes to polar coordinates r, θ, ϕ, with the origin inside the system and the limits of integration 0 to r, 0 to π and 0 to 2π, in which case r is the only limit actually lying on the boundary. The increased simplicity of the properly chosen coordintes arises from the fact that the right hand side of equation (42) is then completely determined solely by the values assumed at the boundary by the quantities $\mathfrak{T}_\mu^1$, $\mathfrak{t}_\mu^1$ etc. and is not dependent on their values within the system.

Having chosen coordinates in the way suggested, the interpretation of equation (42) becomes very simple. The equation now states that the rate of change with time x_4 of the volume integral on the left hand side of the equation is equal to the quantity on the right hand side, whose value is entirely determined by the conditions prevailing at the boundary of the system. The left hand side of the equation can then be interpreted as the rate of change with the time of a component of the total momentum of the system, with $\mu=1, 2, 3$, or the rate of change of the energy of the system, with $\mu=4$; and the right hand side of the equation can be interpreted as the flux of momentum or energy through the boundary.

The use of equation (42) will also be facilitated by the suggested choice of coordinates, when we are interested in some process which takes place within our system under circumstances such that we have definite information as to

the values of the quantities $\mathfrak{T}_\mu^1$, $\mathfrak{t}_\mu^1$ etc. at the boundary of the system, but do not have definite information as to the values they may assume in the interior of the system during the course of the process which interests us. In the following section we shall use coordinates of the kind suggested without further remark.

§10. Application of the Energy-Momentum Principle to the Static States of a System

Having thus obtained an indication as to the interpretation and use of the energy-momentum principle in the case of non-isolated systems, we shall now apply the principle to determine what restriction it would impose on the form of line element within a system which could exist in different static states. To solve this problem we apply the energy-momentum principle to the following process.

We start with a non-isolated system which together with its surroundings is originally in some given static state such that none of the components of the metrical tensor are changing with the time x_4. Without altering the metric or the distribution of matter and radiation outside of the system, we then assume a change to take place in the distribution of matter and energy inside the system in such a way that the system ultimately arrives in some new possible static state. In the absence of the detailed knowledge, which would permit us to describe the exact mechanism of the internal process that takes place, we now inquire into the restrictions which the energy-momentum principle, as applied to the system as a whole, would impose on the changes in the form of line element inside the system which could accompany such a process.

The first condition on the possible changes in the line element is imposed by the hypothesis that the metric and the distribution of matter and radiation outside the system are not to be changed by the process, this hypothesis being introduced since our interest will lie in those changes which could take place solely within the system without affecting anything in the outside surroundings. As an immediate result of the assumption that the metric is not to be changed outside of the system, it is at once evident that the process must produce no change in the values at the boundary of the components $g_{\mu\nu}$ of the metrical tensor and their first differential coefficients $\partial g_{\mu\nu}/\partial x_\alpha$. And as a result of the assumption that the distribution of matter and radiation is not to be changed outside of the system, it is evident that the energy-momentum tensor $T^{\mu\nu}$ will remain unchanged at the boundary since it is completely determined by the distribution of matter and radiation in accordance with the equation of definition

$$T^{\mu\nu} = \rho_0 \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} . \tag{43}$$

The second condition on the possible changes in the line element is imposed by the requirement that the process taking place within the system shall agree with the energy-momentum principle as applied to the system as a whole. This condition is given by our previous equation

$$\frac{\partial}{\partial x_4}\iiint (\mathfrak{T}_\mu^4+\mathfrak{t}_\mu^4)dx_1dx_2dx_3$$
$$=-\iint\left|\mathfrak{T}_\mu^1+\mathfrak{t}_\mu^1\right|_{x_1}^{x_1'}dx_2dx_3-\iint\left|\mathfrak{T}_\mu^2+\mathfrak{t}_\mu^2\right|_{x_2}^{x_2'}dx_1dx_3-\iint\left|\mathfrak{T}_\mu^2+\mathfrak{t}_\mu^3\right|_{x_3}^{x_3'}dx_1dx_2. \tag{44}$$

To apply this equation, we note that at the start of the process when the system is in its original static state, the left hand side of the equation is obviously equal to zero since none of the quantities involved can be changing with the time. Thus at the start of the process the values at the boundary of the quantities $\mathfrak{T}_\mu^1 \cdots \mathfrak{t}_\mu^3$ must be such as to make the right hand side also equal to zero. The quantities $\mathfrak{T}_\mu^1$, $\mathfrak{T}_\mu^2$ and $\mathfrak{T}_\mu^3$, however, are determined by the $g_{\mu\nu}$ and $T^{\mu\nu}$ and the quantities $\mathfrak{t}_\mu^1$, $\mathfrak{t}_\mu^2$ and $\mathfrak{t}_\mu^3$ by the $g_{\mu\nu}$ and $\partial g_{\mu\nu}/\partial x_\alpha$, and hence in accordance with the last paragraph the values which they assume at the boundary will not change during the process. The result is that both sides of equation (44) remain equal to zero throughout the process, and the condition imposed by the energy-momentum principle reduces to the requirement of constant energy and components of momentum for the system as given by the equation

$$\iiint (\mathfrak{T}_\mu^4+\mathfrak{t}_\mu^4)dx_1dx_2dx_3=\text{const.} \tag{45}$$

To investigate the effect of this condition on the possible changes in line element which could occur, we shall now reexpress the integrand by substituting for it the expression given by equation (7) in §3. We thus obtain

$$\iiint \frac{\partial}{\partial x_\gamma}\left(-\mathfrak{g}^{\alpha 4}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_\gamma^{\mu\alpha}}+\frac{1}{2}g_\mu^4\mathfrak{g}^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_\gamma^{\alpha\beta}}\right)dx_1dx_2dx_3=\text{const.} \tag{46}$$

In this equation, however, the suffix γ is a dummy and the term with $\gamma=4$ will be zero at the beginning and end of our process, since by hypothesis the system is at these times a static one and the rate of change of all quantities with respect to the time x_4 is zero. Hence, writing the summation out in full and performing the possible integrations with respect to x_1, x_2 and x_3 which are indicated, we can now express the condition imposed on the form of the line element by stating that for the static states at the beginning and end of the process we must have the relation

$$\begin{aligned}
&\iint\left|-\mathfrak{g}^{\alpha 4}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_1^{\mu\alpha}}+\frac{1}{2}g_\mu^4\mathfrak{g}^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_1^{\alpha\beta}}\right|_{x_1}^{x_1'}dx_2dx_3\\
+&\iint\left|-\mathfrak{g}^{\alpha 4}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_2^{\mu\alpha}}+\frac{1}{2}g_\mu^4\mathfrak{g}^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_2^{\alpha\beta}}\right|_{x_2}^{x_2'}dx_1dx_3\\
+&\iint\left|-\mathfrak{g}^{\alpha 4}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_3^{\mu\alpha}}+\frac{1}{2}g_\mu^4\mathfrak{g}^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_3^{\alpha\beta}}\right|_{x_3}^{x_3'}dx_1dx_2=\text{const.}
\end{aligned} \tag{47}$$

where the limits of integration x_1, x_1' etc. lie on the boundary of the system. The quantities occurring in the integrands of this equation, however, are completely determined by the values of the components $g_{\mu\nu}$ of the metrical tensor and their first differential coefficients, as can be verified from equations already given in this article. Hence the condition imposed by the energy-momentum principle has already been met by our previous requirement necessary to preserve the metric outside that the values at the boundary for the $g_{\mu\nu}$ and their first differential coefficients should not be changed by the process.

Hence, noting the restriction given in §9 as to the kind of coordinate systems that we employ, we can now state the following otherwise general conclusion. Let us start with a non-isolated system, which together with its surroundings is originally in some given static state, and consider that some process then takes place which leaves the metric and the distribution of matter and radiation outside the system unaltered but changes the matter and radiation inside the system in such a way that we finally arrive in some new static state. Assuming no detailed knowledge as to the nature of the internal process that has occurred, but applying the energy-momentum principle to the system as a whole, we then find that the requirements imposed by the energy-momentum principle on the possible changes in line element within the system are to be met by the condition that the components $g_{\mu\nu}$ of the metrical tensor and their first differential coefficients $\partial g_{\mu\nu}/\partial x_\alpha$ are to retain their values unaltered at the boundary.[25]

§11. Conclusion

This concludes the material which it was desired to present in the present article. It is hoped that the general coherence of the treatment and the specific satisfactory result, as to the inclusion of the ordinary Newtonian expression for potential gravitational energy in the case of a fluid sphere in a weak gravitational field, will increase the confidence with which the energy principle is used in general relativity.

Some apology should perhaps be offered for the great length of the two preceding sections on the application of the energy principle to the changes that may take place within a limited region which forms part of a larger system. There are, however, a number of points connected with the development which have seemed puzzling enough to warrant a detailed exposition and the final conclusion is one of considerable usefulness.

It should perhaps also be remarked that we have not treated in the foregoing any questions which involve the energy of the closed universe as a whole since these deserve separate consideration.[26]

[25] In connection with the formulation of this section, I have been greatly helped by discussions with my colleague Dr. J. Robert Oppenheimer, for which I wish to thank him, also in this place.

[26] See Einstein, Berl. Ber. 1918, p. 452, and Tolman, Proc. Nat. Acad. **14**, 348 (1928).

ON THE USE OF THE ENTROPY PRINCIPLE IN GENERAL RELATIVITY

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Abstract

The main purpose of this article is to use the extension of thermodynamics to general relativity, previously proposed by the author, to obtain expressions which will give the criteria for the thermodynamic equilibrium of a static gravitating system in a readily applicable mathematical form. After restating the principle chosen by the author as the general relativity analogue of the second law of thermodynamics, and showing once more that it is a natural covariant generalization of the ordinary second law of thermodynamics, the principle is then applied to finite systems in general and to adiabatic systems having no flux of matter or heat at the boundary. The mathematical conditions for thermodynamic equilibrium are then obtained for the case of any finite static system, and a specially useful form for these conditions is obtained for the case that the system has spherical symmetry.

§1. Introduction

In several previous articles, I have attempted an extension of thermodynamics to general relativity[1] and have tried to make certain applications of this extension.[2] The main purpose of the present article is to prepare for certain further applications which I propose to make.

The postulate, which must be taken in work of this kind as the general relativity analogue of the ordinary first law of thermodynamics, is evidently Einstein's generalized energy-momentum principle, which reduces in flat space-time to the ordinary laws of the conservation of energy and momentum, and is a principle which certainly must not be violated by any thermodynamic changes which may take place. The use of this principle has already been discussed in some detail in the preceding article in this journal,[3] and, those conclusions drawn from it, which will be necessary for the present considerations.

The postulate which was chosen as the general relativity analogue of the second law of thermodynamics was a new one, which was justified, so far as may be, by showing it to be a natural covariant generalization of the ordinary second law of thermodynamics in flat space-time. In the present article we shall be especially interested in the method of applying this principle to determine the equilibrium conditions for a finite system in a static state.

[1] Tolman, Proc. Nat. Acad. **14,** 268 (1928); ibid. **14,** 701 (1928).
[2] Tolman, Proc. Nat. Acad. **14,** 348 (1928); ibid. **14,** 353 (1928).
[3] Tolman, Phys. Rev. **35,** 875 (1930).
[4] See reference (3) last paragraph of §10.

In the immediately following section, §2, we shall again state the postulate chosen as the general relativity analogue of the second law of thermodynamics in the form which it assumes for an infinitesimal region, and show again by way of review that it is a natural covariant generalization of the ordinary second law of thermodynamics valid in flat space-time. In §3, we shall obtain by integration the form taken by the principle in the case of a finite system in general, and then more especially in the case of an adiabatic system having no flux of matter or heat at the boundary. Following this we shall consider, in §4, the conditions for thermodynamic equilibrium in the case of a finite static system, and finally, in §5, we shall consider a specific form in which these conditions for equilibrium can be put in case the system under consideration has spherical symmetry.

§2. The Generalized Second Law of Thermodynamics

To state the postulate which was taken as the general relativity analogue of the second law of thermodynamics, we shall first define the *entropy vector* at a given point in space-time, by the equation

$$S^\mu = \phi_0 \frac{dx_\mu}{ds} \tag{1}$$

where ϕ_0 is the *proper density of entropy* at the point in question as measured by a local observer, and dx_μ/ds is the *macroscopic velocity* of matter at that point. Corresponding to this vector, we also have the *entropy vector density* given by the equation

$$\mathfrak{S}^\mu = S^\mu \sqrt{-g} = \phi_0 \sqrt{-g} \frac{dx_\mu}{ds} . \tag{2}$$

The second law postulate can then be stated in the form

$$\frac{\partial \mathfrak{S}^\mu}{\partial x_\mu} dx_1 dx_2 dx_3 dx_4 \geqq \frac{dQ_0}{T_0} \tag{3}$$

where dQ_0 is the *heat measured in proper coordinates* flowing through the boundary into the infinitesimal region and during the infinitesimal time denoted by $dx_1 dx_2 dx_3 dx_4$, and T_0 is the *proper temperature* at the boundary.

To show that expression (3) is covariant, we rewrite it by a well-known transformation in the form

$$(S^\mu)_\mu \sqrt{-g} dx_1 dx_2 dx_3 dx_4 \geqq \frac{dQ_0}{T_0} . \tag{4}$$

The quantity $(S^\mu)_\mu$, however, is the contracted covariant derivative of S^μ and is known to be an invariant, while $\sqrt{-g} dx_1 dx_2 dx_3 dx_4$ and dQ_0/T_0 are also obviously invariants so that both sides of expression (4) are tensors of rank zero, and the requirement of covariance is met in the simplest possible way.

To show that expression (3) reduces to the ordinary requirements of the second law in the limiting case of flat space-time, we first rewrite it with the help of (2) in the form

$$\frac{\partial}{\partial x_\mu}\left(\phi_0\sqrt{-g}\,\frac{dx_\mu}{ds}\right)dx_1dx_2dx_3dx_4 \geqq \frac{dQ_0}{T_0}\,. \tag{5}$$

In flat space-time, however, using Galilean coordinates x, y, z and t, we shall have $\sqrt{-g}=1$, and writing out the indicated summation in full, we obtain with some rearrangement in the order of terms

$$\frac{\partial}{\partial t}\left(\phi_0\frac{dt}{ds}\right)dxdydzdt$$
$$\geqq -\left[\frac{\partial}{\partial x}\left(\phi_0\frac{dx}{ds}\right)+\frac{\partial}{\partial y}\left(\phi^0\frac{dy}{ds}\right)+\frac{\partial}{\partial z}\left(\phi_0\frac{dz}{ds}\right)\right]dxdydzdt+\frac{dQ_0}{T_0}$$

and this can evidently be rewritten as

$$\frac{\partial}{\partial t}\left(\phi_0\frac{dt}{ds}\right)dxdydzdt$$
$$\geqq\left[\frac{\partial}{\partial x}\left(\phi_0\frac{dt}{ds}\,\frac{dx}{dt}\right)+\frac{\partial}{\partial y}\left(\phi_0\frac{dt}{ds}\,\frac{dy}{dt}\right)+\frac{\partial}{\partial z}\left(\phi_0\frac{dt}{ds}\,\frac{dz}{dt}\right)\right]dxdydzdt+\frac{dQ_0}{T_0}\,. \tag{6}$$

In accordance, however, with the special theory of relativity, valid in flat space-time, entropy is an invariant for the Lorentz transformation, so that entropy density will be affected by the Lorentz-Fitzgerald factor of contraction ds/dt in such a way that we can make the substitution

$$\phi=\phi_0\frac{dt}{ds} \tag{7}$$

where ϕ is the density of entropy in the particular set of Galilean coordinates that are being used. Furthermore, since heat and temperature have the same transformation factors on the basis of the special theory, we may also substitute

$$\frac{dQ}{T}=\frac{dQ_0}{T_0}\,. \tag{8}$$

Hence, using u, v, w to denote the components of ordinary velocity dx/dt etc. we can finally rewrite expression (6) in the form

$$\frac{\partial\phi}{\partial t}dxdydzdt\geqq-\left[\frac{\partial}{\partial x}(\phi u)+\frac{\partial}{\partial y}(\phi v)+\frac{\partial}{\partial z}(\phi w)\right]dxdydzdt+\frac{dQ}{T}\,. \tag{9}$$

This expression, however, evidently states the essence of the ordinary second law of thermodynamics, since it requires that the actual increase of entropy occurring in the time dt in the infinitesimal volume $dx\,dy\,dz$ cannot be less

than the total entropy brought in from the outside by the flux of matter and the flow of heat.

Our postulate as to the general relativity analogue of the second law has thus been justified both by the fact of its expression in covariant form and by its reduction in the limiting case of flat space-time to the ordinary second law of thermodynamics. The justification, thus presented, is of course in no sense a complete proof of the validity of the postulate taken. Covariance and agreement with the form of the second law valid in the special theory of relativity are necessary but not sufficient requirements for determining the new form of the second law. The new postulate must be regarded as a real generalization containing an element not present in the special theory of relativity, and the ultimate complete justification of the postulate must be dependent on the agreement between the conclusions that can be drawn from it and actual experimental or observational facts.

§3. Application of the Entropy Principle to Finite Systems

To apply the new principle to the changes taking place in a finite system, let us start with the principle in the form given by expression (5), and taking x_1, x_2 and x_3 as being the space-like coordinates, integrate over the spatial region of interest. If we carry out such an integration, using coordinates such that the limits of integration necessary to include the whole system fall on the actual boundary which separates the system from its surroundings, it is evident that the summation of dQ_0/T_0 over the interior of the system will cancel out, since any heat entering a given element of volume is abstracted from neighboring elements, so that we shall only have to consider the heat entering the system from its surroundings. Hence dividing equation (5) through by dx_4, writing out the indicated summation, and performing the suggested integration, we obtain with some rearrangement in the order of terms

$$\frac{\partial}{\partial x_4}\iiint\left(\phi_0\sqrt{-g}\,\frac{dx_4}{ds}\right)dx_1dx_2dx_3$$

$$\geqq -\iiint\left[\frac{\partial}{\partial x_1}\left(\phi_0\sqrt{-g}\,\frac{dx_1}{ds}\right)+\frac{\partial}{\partial x_2}\left(\phi_0\sqrt{-g}\,\frac{dx_2}{ds}\right)\right.$$

$$\left.+\frac{\partial}{\partial x_3}\left(\phi_0\sqrt{-g}\,\frac{dx_3}{ds}\right)\right]dx_1dx_2dx_3+\sum\left(\frac{1}{T_0}\,\frac{dQ_0}{dx_4}\right)_{\text{Boundary}}.$$

The last term on the right hand side of this expression is the total value taken over the boundary of the system of the quantity $(1/T_0)\,(dQ_0/dx_4)$, and by performing the indicated integrations the other terms on this side of the expression can also be seen to depend solely on quantities whose values are determined by conditions at the boundary, provided we continue to use, as suggested above, a set of coordinates so chosen that the limits of integration necessary to include the whole of the system actually lie on the boundary. We obtain

$$\frac{\partial}{\partial x_4}\int\int\int\left(\phi_0\sqrt{-g}\frac{dx_4}{ds}\right)dx_1dx_2dx_3 \geqq \int\int\left|\phi_0\sqrt{-g}\frac{dx_1}{ds}\right|_{x_1}^{x_1'}dx_2dx_3$$
$$-\int\int\left|\phi_0\sqrt{-g}\frac{dx_2}{ds}\right|_{x_2}^{x_2'}dx_1dx_3-\int\int\left|\phi_0\sqrt{-g}\frac{dx_3}{ds}\right|_{x_3}^{x_3'}dx_1dx_2 \tag{10}$$
$$+\Sigma\left(\frac{1}{T_0}\frac{dQ_0}{dx_4}\right)_{\text{Boundary}}$$

where the limits of integration at the boundary of the system are denoted by x_1, x_1' etc.

This expression (10) may be regarded as a general statement of the second law of thermodynamics as applied to finite systems, and defining the entropy of the system by the equation

$$S=\int\int\int\left(\phi_0\sqrt{-g}\frac{dx_4}{ds}\right)dx_1dx_2dx_3 \tag{11}$$

the expression can be interpreted as giving the relation which must hold between the rate at which the entropy of a finite system is changing with the "time" x_4, and those conditions existing at the boundary which determine the flux of matter and the flow of heat.

For the case of an adiabatic system with no flow of heat through the boundary, and in addition with the quantities dx_1/ds, dx_2/ds and dx_3/ds equal to zero at the boundary, so that there is no flux of matter between the system and its surroundings, expression (10) reduces to

$$\frac{\partial}{\partial x_4}\int\int\int\left(\phi_0\sqrt{-g}\frac{dx_4}{ds}\right)dx_1dx_2dx_3 \geqq 0. \tag{12}$$

In accordance with this expression, the entropy of an adiabatic system of the kind described can only increase or remain constant with increases in the time x_4.

§4. Thermodynamic Equilibrium in a Static System

We shall now investigate the conditions for thermodynamic equilibrium in a static system. To do this we must examine the changes which could take place from one static state to another without violating either the energy-momentum principle or the entropy principle as applied to the system as a whole.

Consider a system which together with its surroundings is originally in some given static state, such that none of the components $g_{\mu\nu}$ of the metrical tensor are changing with the time, and furthermore such that there is no flow of heat nor macroscopic flux of matter or radiation at any point. Without alteration in the metric or the distribution of matter and radiation outside of the system we then assume some change to take place in the distribution of matter and radiation inside the boundary in such a way that the system ultimately arrives in some new possible static state. Assuming no detailed

knowledge of the exact nature of the internal process which occurs, we now inquire into the restrictions which the energy-momentum principle and the entropy principle applied to the system as a whole would impose on the change in state.

In accordance with a conclusion obtained in my previous article on the energy-momentum principle,[4] the restrictions imposed by this principle on the possible changes in line element within the system are to be met by the condition that the components $g_{\mu\nu}$ of the metrical tensor and their first differential coefficients $\partial g_{\mu\nu}/\partial x_\alpha$ are to retain their values unaltered at the boundary. These restrictions, coming from considerations of the energy-momentum principle, must be applied as part of the thermodynamic criteria for determining the possible changes in state.

Turning now to the entropy principle, we note that the process under consideration has been so chosen that the change is an adiabatic one of the kind described in the preceding section, since by hypothesis the flow of heat and macroscopic flux of matter are everywhere zero at the start and remain so at the boundary while the process is under way; hence we can at once apply expression (12) to the process. We thus obtain as the restriction imposed by the entropy principle the requirement that the entropy as defined by equation (11) shall not be decreased by the process. This restriction must be applied as giving the remaining thermodynamic criteria for determining the possible changes in state.

The considerations of the last two paragraphs immediately make it evident that the condition for the thermodynamic equilibrium of a static system, with no flow of heat or flux of matter at any point, is that the entropy of the system as given by equation (11) shall be the maximum that can be obtained without violating the boundary conditions furnished from considerations of the energy-momentum principle. Stating this conclusion more specifically by the use of the calculus of variations, we may now give as the condition of thermodynamic equilibrium in a static system of the kind described above

$$\delta \iiint \phi_0 \sqrt{-g} \frac{dx_4}{ds} dx_1 dx_2 dx_3 = 0 \tag{13}$$

under the subsidiary condition holding *at the boundary of the system*

$$\delta g_{\mu\nu} = \delta \left(\frac{\partial g_{\mu\nu}}{\partial x_\alpha} \right) = 0 \tag{14}$$

where it is to be remembered that the conclusions have been derived using a system of coordinates such that the limits of integration necessary to include the whole of the system of interest fall on the actual boundary which separates the system from its surroundings.

§5. Equilibrium in a Static System Having Spherical Symmetry

As just mentioned the conditions given by equations (13) and (14) have been derived using a system of coordinates such that the limits of integration

necessary to include the whole of the system fall on the actual boundary separating it from its surroundings. In the case of a system having spherical symmetry, it is possible, however, to translate these results into a system of polar coordinates, and thus put them into a more convenient form for use.

Let us take a static system of the kind discussed above, with no flow of heat nor macroscopic flux of matter or radiation at any point, and having spherical spatial symmetry, and let us initially make use of a set of coordinates x, y, z, t with the center of symmetry at the origin of the three equivalent spatial axes x, y and z. Such a set of coordinates is of the kind used in deriving the restrictions given by equations (13) and (14).

The line element for our system in these coordinates can evidently be written in the form

$$ds^2 = -e^{\mu}(dx^2+dy^2+dz^2) + e^{\nu}dt^2 \tag{15}$$

where the exponents μ and ν are independent of the time t, and on account of the spherical symmetry depend on the coordinates x, y and z in such a way that they are expressible as functions of $(x^2+y^2+z^2)^{1/2}$.

In accordance with this line element we have

$$g_{11}=g_{22}=g_{33}=-e^{\mu} \qquad g_{44}=e^{\nu}$$
$$\sqrt{-g}=e^{\frac{3\mu+\nu}{2}} \tag{16}$$

and since there is no macroscopic flux of matter or radiation, we have the value zero for all the macroscopic velocities dx_μ/ds except for the case $\mu=4$, and then have

$$\frac{dx_4}{ds}=\frac{dt}{ds}=e^{-\nu/2}. \tag{17}$$

Substituting the values given by equations (16) and (17) into equations (13) and (14) we then have as the requirement for thermodynamic equilibrium in our present coordinates

$$\delta\int\int\int \phi_0 e^{3\mu/2}dxdydz=0 \tag{18}$$

under the subsidiary condition holding at the boundary of the system

$$\delta\mu=\delta\left(\frac{\partial\mu}{\partial x_\alpha}\right)=\delta\nu=\delta\left(\frac{\partial\nu}{\partial x_\alpha}\right)=0. \tag{19}$$

These requirements, however, can now easily be translated into polar coordinates r, θ and ϕ by setting

$$\begin{aligned} x&=r\sin\theta\cos\phi \\ y&=r\sin\theta\sin\phi \\ z&=r\cos\theta \end{aligned} \tag{20}$$

and noting that the condition of spherical symmetry makes it possible to take μ and ν as functions of r alone

$$\mu=\mu(r) \qquad \nu=\nu(r). \tag{21}$$

The requirements for thermodynamic equilibrium then evidently become

$$\delta\iiint \phi_0 e^{3\mu/2} r^2 \sin\theta dr d\vartheta d\phi = 0 \tag{22}$$

under the subsidiary condition

$$\delta\mu=\delta\mu'=\delta\nu=\delta\nu'=0 \tag{23}$$

where the primes indicate differentiation with respect to r, and the limitation given by (23) is to be applied at the actual boundary separating the system from its surroundings rather than at the limits of integration which must be given to the new variables in order to include the region of interest.

Finally if we take the region of interest as being a spherical shell contained between the constant radii r_1 and r_2, we can evidently rewrite equations (22) and (23) in the form

$$\delta\left[4\pi\int_{r_1}^{r_2} \phi_0 e^{3\mu/2} r^2 dr\right]=0 \tag{24}$$

under the subsidiary condition

$$\delta\mu=\delta\mu'=\delta\nu=\delta\nu'=0 \quad (\text{at } r_1 \text{ and } r_2). \tag{25}$$

It is believed that this form of the conditions of equilibrium will be found an easy and useful one to employ.

ON THE WEIGHT OF HEAT AND THERMAL EQUILIBRIUM IN GENERAL RELATIVITY

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Abstract

In accordance with the special theory of relativity all forms of energy, including heat, have inertia and hence in accordance with the equivalence principle also have weight. The purpose of the present article is to investigate the thermodynamic implications of the idea that heat has weight. In particular an investigation is made to see if a temperature gradient is a necessary accompaniment of thermal equilibrium in a gravitational field, in order to prevent the flow of heat from regions of higher to those of lower gravitational potential.

A preliminary non-rigorous treatment of this problem is first given by attempting to modify the classical thermodynamics only to the extent of associating with each intrinsic quantity of energy an additional amount of potential gravitational energy. In this way an expression is obtained for increase in equilibrium temperature with decrease in gravitational potential which, however, could in any case only be correct as a first approximation in a weak gravitational field. A discussion of the uncertainties and lack of rigor of this preliminary treatment is then given and the necessity pointed out for a rigorous treatment based on the principles of general relativity.

A rigorous relativistic treatment is then undertaken using the extension of thermodynamics to general relativity previously presented by the author. The system to be treated is taken as a static spherical distribution of perfect fluid which has come to gravitational and thermodynamic equilibrium. The principles of relativistic mechanics are first applied to such a system in order to obtain results needed in the later work. And it is then shown that these *mechanical* principles themselves are sufficient to determine the temperature distribution as a function of potential in the simple case of black-body radiation. The principles of relativistic thermodynamics are then applied to this same case of pure black-body radiation and the same expression for temperature as a function of potential obtained by the *thermodynamic* as by the mechanical treatment. This may be regarded as giving some measure of check on the validity of the proposed relativistic thermodynamics.

Following this, a thermodynamic treatment is given for the temperature distribution in the more general case of matter and radiation and a result found which harmonizes with that for radiation alone. A treatment is then given to the distribution of a perfect monatomic gas in a gravitational field both on the assumption that the total number of atoms must remain constant and on the assumption of the ready interconvertibility of matter and radiation. In the latter case the same dependence of concentration on temperature is obtained as was found by Stern and by the author for the case of flat space-time.

Using a system of coordinates such that the line element for the sphere of fluid takes the form

$$ds^2 = -e^{\alpha}(dr^2+r^2d\theta^2+r^2\sin^2\theta d\phi^2)+e^{\nu}dt^2$$

the general result for the relation between gravitational potential and equilibrium temperature T_0 as measured by a local observer in proper coordinates can be given by the equation

$$\frac{d\,lnT_0}{dr} = -\frac{1}{2}\frac{d\nu}{dr}$$

This equation reduces in the case of a weak field to that obtained by the preliminary non-rigorous treatment, and gives a very small change of temperature with position in fields of ordinary intensity. The result, however, is one of great theoretical interest, since constant temperature throughout any system which has come to thermal equilibrium has hitherto been regarded as an inescapable thermodynamic conclusion. It is also not out of the question that the effect might sometime be of experimental or observational importance.

§1. Introduction

ONE of the most important results of the special theory of relativity was the relation between the total energy of a system U and its inertial mass m, given by Einstein's equation

$$U = mc^2 \tag{1}$$

where c is the velocity of light. In accordance with this equation we must ascribe the property of inertia to energy. For ordinary matter, however, we are in the possession of very exact experimental results showing a proportionality between inertia and weight, and hence the question at once arises whether we must also ascribe to energy the property of weight.

As early as 1911, in developing those ideas which finally led to the general theory of relativity, Einstein[1] considered this question, as to the weight of energy, and showed by a simple application of the equivalence hypothesis that the property of weight must indeed also be ascribed to energy if we are to maintain the postulated equivalence between behavior in a homogeneous gravitational field and behavior with reference to a set of uniformly accelerated axes. The later more complete developments of the general theory of relativity have shown that the Newtonian concept of the weight of a body as a force acting on it when placed in a gravitational field, is an idea which is only suitable for the treatment of slow-moving particles in weak gravitational fields. Nevertheless, these more complete developments of the general theory of relativity have completely confirmed the fundamental nature of the idea that weight must be ascribed to energy, since they have shown in any case that all forms of energy will be subject to the same gravitational action when placed under the same conditions in a gravitational field. Furthermore, in the case of weak enough fields and slow enough motions so that the Newtonian concepts may still be taken as approximately valid, the general theory of relativity has shown that the gravitational force F acting on any quantity of energy U will be given as would be expected by the simple equation

[1] Einstein, Ann. d. Physik **35,** 898 (1911).

$$F=(U/c^2)g \tag{2}$$

where g is the acceleration due to gravity.

If we accept the conclusion that energy has weight, it is evident that we must also ascribe weight to energy in the form of heat, and hence must expect to find thermodynamic consequences of the new idea. Thus considering for example cases where the Newtonian approximation is valid, we might expect the flow of heat from a place of higher to a place of lower gravitational potential to be accompanied by a decrease in potential energy, and this in turn would lead us to suspect that the condition of thermal equilibrium in a gravitational field might involve higher temperatures at the lower gravitational levels in order to prevent any thermal flow. It is the purpose of the present article to investigate the thermodynamic consequences of this idea that heat has weight, making use of principles obtained in an extension of thermodynamics to general relativity which I have already given.[2]

In the immediately following section, §2, we shall first consider a preliminary treatment of temperature equilibrium in the case of a system in such a weak gravitational field that we shall feel warranted in trying to apply the Newtonian concept of gravitation as a first approximation. And in §3, we shall examine the inadequacies of this preliminary treatment and show the necessity for the more rigorous treatments to follow. In §4, we shall then prepare for the rigorous general relativity treatment by applying the principles of relativistic mechanics to a spherical distribution of perfect fluid to obtain results which will be needed in the later developments. And in §5, we shall show that these purely mechanical results are alone sufficient to determine the temperature distribution in the simple case of a spherical distribution of pure radiation. In §6, we shall then briefly restate that result of the earlier extension of thermodynamics to general relativity which is necessary for our present considerations and then apply it in §7 to this same special case of pure radiation, and show that the same results are also obtained from the thermodynamic as from the purely mechanical treatment; this may be regarded as furnishing a partial confirmation of the correctness of the new system of relativistic thermodynamics. Following this, in §8, we shall use our relativistic thermodynamics to obtain a general equation for the distribution of temperature in any spherical mass of gravitating fluid, which has come to equilibrium. In §9, we shall then consider the equilibrium distribution of matter in a gravitational sphere of fluid; in particular the cases of a perfect monatomic gas, both when in equilibrium with radiation and when the total number of atoms is constant, will be treated. Finally in §10, we shall make some concluding remarks.

§2. Preliminary Treatment of Temperature Equilibrium in a Weak Gravitational Field

To obtain a preliminary non-rigorous treatment of the temperature equilibrium in a weak gravitational field, we shall endeavor to apply the

[2] Tolman, Proc. Nat. Acad. **14**, 268 (1928); ibid. **14**, 701 (1928); This Journal, 896, ibid.

principles of the classical theomodynamics, modified only by assuming that the force of gravity will act on any quantity of energy U as though it had a weight, in the Newtonian sense, corresponding to its inertial mass U/c^2. Under these circumstances a quantity of energy which has the intrinsic magnitude U, when measured at the zero of gravitational potential at a great distance from bodies producing a gravitational field, will be assumed to have associated with it the potential energy $U\Psi/c^2$ when brought to a point where the gravitational potential has the value Ψ.

Consider now an isolated sphere of material which is held together by its own gravitational attraction, but has a small enough mass so that the gravitational field is everywhere weak. In accordance with the classical thermodynamics, this system should be in equilibrium provided it has the maximum entropy S consistent with its total energy U. To determine the temperature distribution which corresponds to these conditions, let us then consider a small variation in temperature distribution, leaving unaltered, however, the amount of substance of each component in each element of volume dV. For the variation in total entropy we shall write

$$\delta S = \int \frac{\delta u}{T} dV \tag{3}$$

where T is the temperature at the point where the element of volume dV is located, δu is the change in the intrinsic energy density at that point produced by the variation in temperature, and the integration is to be taken over the whole volume of the system. On the other hand for the variation in the total energy of the system, we shall write

$$\delta U = \int \left(1 + \frac{\Psi}{c^2}\right) \delta u \, dV \tag{4}$$

where Ψ is the gravitational potential at the point in question.

Setting equation (3) equal to zero as the condition that the entropy be a maximum, and equation (4) equal to zero as the subsidiary condition of constant energy, and combining by the method of Lagrange, we obtain

$$\int \left[\frac{1}{T} - \lambda\left(1 + \frac{\Psi}{c^2}\right)\right] \delta u \, dV = 0 \tag{5}$$

where λ is a constant undetermined multiplier, and this equation can only be true for arbitrary variations δu, if we have

$$\frac{1}{T} = \lambda\left(1 + \frac{\Psi}{c^2}\right) \tag{6}$$

which is the desired expression giving the distribution of the temperature T throughout the system as a function of the gravitational potential Ψ.

Differentiating this equation with respect to the radius r, to obtain an expression for the rate of change of the temperature with distance from the center of the gravitating sphere, we have

$$-\frac{1}{T^2}\frac{dT}{dr}=\frac{\lambda}{c^2}\frac{d\Psi}{dr}$$

and substituting the expression for λ which can be obtained from (6), we obtain

$$\frac{d\ln T}{dr}=-\frac{(1/c^2)(d\Psi/dr)}{1+\Psi/c^2}=-\frac{d}{dr}\ln\left(1+\frac{\Psi}{c^2}\right) \tag{7}$$

or since by hypothesis the field is weak enough so that Ψ/c^2 is small compared with unity we have approximately

$$\frac{d\ln T}{dr}=-\frac{1}{c^2}\frac{d\Psi}{dr}=-\frac{g}{c^2} \tag{8}$$

where g is the acceleration due to gravity.

For the case of a field of vanishing gravitational intensity with g negligible, the result degenerates into the usual condition for thermal equilibrium, $T=$constant. Furthermore, owing to the magnitude of the velocity of light the percentage change in temperature with height would be very small in fields of any ordinary intensity. Thus in a gravitational field having the strength of that at the surface of the earth we should have approximately

$$\frac{d\ln T}{dr}=-10^{-17}\ \text{cm}^{-1}.$$

§3. Inadequacy of the Preliminary Treatment

The foregoing treatment contains of course many inadequacies and uncertainties, which can only be removed by a rigorous treatment of the problem from the point of view of general relativity. In the first place, in accordance with the classical thermodynamics, we have assumed maximum entropy and constant energy as the criteria of equilibrium for an isolated system, without any certain knowledge as to the form or even the validity of such principles in the presence of a gravitational field. Equation (3) for the entropy assumes it to depend on what we have called the intrinsic energy but the justification for this is by no means clear. Equation (4) for the energy, on the other hand, even if satisfactory for the case of weak gravitational fields,[3] can certainly not be regarded as correct in general when we recall the great modifications in the nature of the energy principle which have to be introduced in the theory of general relativity. Furthermore, it should be noted that we have given no very clear definition of the quantities temperature T and intrinsic energy density u which occur in the equations, although we might perhaps guess that we should take the values of these quantities as measured by local observers using proper coordinates. In addition, even the interpretation of the quantity dV appears dubious when we recall the differences between pro-

[3] See §8 in the article already referred to, This Journal, 888, for a satisfactory approximate treatment of the energy of a sphere of perfect fluid in a weak gravitational field.

per volume and coordinate volume which occur in the general theory of relativity.

It is hence abundantly evident that we cannot regard the results of the preceding section as having any certainty of validity, unless indeed we can show them to be an approximation in weak fields for conclusions which can be obtained from a more rigorous general relativity treatment. In what follows we shall now turn our attention to the general relativity treatment of the distribution of temperature and matter in a sphere of gravitating fluid which has come to thermodynamic equilibrium.

§4. The Relativity Mechanics of a Spherical Distribution of Perfect Fluid

As a preparation for our later work we must first consider the application of the mechanics of general relativity to a static distribution of perfect fluid having spherical symmetry. For a sufficiently general line element for such a system we may evidently write

$$ds^2 = -e^{\mu}(dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2) + e^{\nu} dt^2 \tag{9}$$

where the conditions that the system is to be static and spherically symmetrical are fulfilled if μ and ν can be taken as functions of r alone.

The components of the metrical tensor corresponding to this line element are evidently

$$\begin{aligned} &g_{11} = -e^{\mu}, \quad g_{22} = -e^{\mu} r^2, \quad g_{33} = -e^{\mu} r^2 \sin^2\theta, \quad g_{44} = e^{\nu} \\ &g^{11} = -e^{-\mu}, \quad g^{22} = -\frac{e^{-\mu}}{r^2}, \quad g^{33} = -\frac{e^{-\mu}}{r^2 \sin^2\theta}, \quad g^{44} = e^{-\nu} \\ &g_{\rho\sigma} = g^{\rho\sigma} = 0 \quad (\rho \neq \sigma) \qquad \sqrt{-g} = e^{\frac{3\mu+\nu}{2}} r^2 \sin\theta \end{aligned} \tag{10}$$

and the components of the contracted Riemann-Christoffel tensor corresponding to this metrical tensor have already been worked out and are known to have the values[4]

$$\begin{aligned} G_{11} &= \mu'' + \frac{\nu''}{2} + \frac{\mu'}{r} - \frac{\mu'\nu'}{4} + \frac{\nu'^2}{4} \\ G_{22} &= \frac{3}{2} r\mu' + \frac{r\nu'}{2} + \frac{r^2\mu''}{2} + \frac{r^2\mu'^2}{4} + \frac{r^2\mu'\nu'}{4} \\ G_{33} &= G_{22} \sin^2\theta \\ G_{44} &= -e^{\nu-\mu}\left[\frac{\nu''}{2} + \frac{\nu'}{r} + \frac{\mu'\nu'}{4} + \frac{\nu'^2}{4}\right] \\ G_{\rho\sigma} &= 0 \qquad (\rho \neq \sigma) \end{aligned} \tag{11}$$

[4] See Eddington, "The Mathematical Theory of Relativity," Cambridge 1923. The results in question can be obtained by setting $\lambda = \mu$ in Eddington's equations (43.5).

where the primes indicate differentiation with respect to r. Raising suffixes with the help of the values of the metrical tensor (10), and substituting into the fundamental equation

$$-8\pi T_\sigma^\rho = G_\sigma^\rho - \tfrac{1}{2} g_\sigma^\rho G \tag{12}$$

which connects the energy-momentum tensor T_σ^ρ with the metric we can then obtain, after a simple calculation, for the separate components of T_σ^ρ

$$\begin{aligned}
-8\pi T_1^1 &= e^{-\mu}\left[\frac{\mu'+\nu'}{r} + \frac{\mu'\nu'}{2} + \frac{\mu'^2}{4}\right] \\
-8\pi T_2^2 &= -8\pi T_3^3 = e^{-\mu}\left[\frac{\mu''+\nu''}{2} + \frac{\mu'+\nu'}{2r} + \frac{\nu'^2}{4}\right] \\
-8\pi T_4^4 &= e^{-\mu}\left[\mu'' + \frac{2\mu'}{r} + \frac{\mu'^2}{4}\right].
\end{aligned} \tag{13}$$

On the other hand in the case of a perfect fluid the energy tensor is known to depend on the properties of the fluid in accordance with the equation[5]

$$T_{00} = (\rho_{00} + p_0)\frac{dx_\rho}{ds}\frac{dx_\sigma}{ds} - g^{\rho\sigma} p_0 \tag{14}$$

where ρ_{00} is the proper *macroscopic* density of energy in the fluid, p_0 its proper pressure and the quantities dx_ρ/ds are *macroscopic* "velocities." Since we assume a static condition in our fluid, these "velocities" will all be zero except for the case ρ or $\sigma = 4$, and in accordance with the line element (9) will then have the value $dx_4/ds = e^{-\nu/2}$. Hence noting the values for $g^{\rho\sigma}$ given by equations (10) we obtain for the separate components of $T^{\rho\sigma}$

$$T^{11} = e^{-\mu} p_0, \qquad T^{22} = \frac{e^{-\mu}}{r^2} p_0, \qquad T^{33} = \frac{e^{-\mu}}{r^2 \sin^2\theta} p_0, \qquad T^{44} = e^{-\nu}\rho_{00} \tag{15}$$

or lowering suffixes with the help of the metrical tensor (10) we have

$$T_1^1 = T_2^2 = T_3^3 = -p_0 \qquad T_4^4 = \rho_{00}. \tag{16}$$

Comparing these results with those given by equations (13) we can now write

$$p_0 = \frac{e^{-\mu}}{8\pi}\left[\frac{\mu'+\nu'}{r} + \frac{\mu'\nu'}{2} + \frac{\mu'^2}{4}\right] \tag{17}$$

$$p_0 = \frac{e^{-\mu}}{8\pi}\left[\frac{\mu''+\nu''}{2} + \frac{\mu'+\nu'}{2r} + \frac{\nu'^2}{4}\right] \tag{18}$$

$$\rho_{00} = -\frac{e^{-\mu}}{8\pi}\left[\mu'' + \frac{2\mu'}{r} + \frac{\mu'^2}{4}\right] \tag{19}$$

[5] See Eddington, reference 4, equations (54.81) and (54.82).

as expressions connecting the proper pressure p_0 and proper macroscopic density ρ_{00} with the metric. The reason that we obtain two separate expressions (17) and (18) connecting the pressure with the metric lies in the fact that the line element (9) with which we have started is sufficiently general to apply to any static distribution having spherical symmetry, while our later assumption of a perfect fluid involves at each point of the fluid an equality between the stresses in the radial and tangential directions.

Adding equations (17), (19), and (18) taken twice we obtain

$$(\rho_{00}+3p_0)=\frac{e^{-\mu}}{8\pi}\left(\nu''+\frac{2\nu'}{r}+\frac{\mu'\nu'}{2}+\frac{\nu'^2}{2}\right)$$

and this can be rewritten in a form which will later prove useful

$$8\pi(\rho_{00}+3p_0)e^{\frac{3\mu+\nu}{2}}r^2=e^{\frac{\mu+\nu}{2}}\left(\nu''+\frac{2\nu'}{r}+\frac{\mu'\nu'}{2}+\frac{\nu'^2}{2}\right)r^2=\frac{d}{dr}\left(e^{\frac{\mu+\nu}{2}}\nu' r^2\right). \quad (20)$$

We are now ready to apply the principles of mechanics to our system, in accordance with the fundamental equation of relativity mechanics which can be written in the form.[6]

$$\frac{\partial \mathfrak{T}_\sigma^\rho}{\partial x_\rho}-\frac{1}{2}\mathfrak{T}^{\alpha\beta}\frac{\partial g_{\alpha\beta}}{\partial x_\sigma}=0 \quad (21)$$

Considering first the case $\sigma=1$, substituting values for the tensor *densities* of energy and momentum obtained from (15) and (16) through multiplication by $\sqrt{-g}$, and substituting for $g_{\alpha\beta}$ from (10), we can write

$$\frac{\partial}{\partial r}(-p_0\sqrt{-g})-\frac{1}{2}(e^{-\mu}p_0\sqrt{-g})\frac{\partial}{\partial r}(-e^{\mu})-\frac{1}{2}\left(\frac{e^{-\mu}}{r^2}p_0\sqrt{-g}\right)\frac{\partial}{\partial r}(-e^{\mu}r^2)$$
$$-\frac{1}{2}\left(\frac{e^{-\mu}}{r^2\sin^2\theta}p_0\sqrt{-g}\right)\frac{\partial}{\partial r}(-e^{\mu}r^2\sin^2\theta)-\frac{1}{2}(e^{-\nu}\rho_{00}\sqrt{-g})\frac{\partial}{\partial r}(e^{\nu})=0$$

and substituting the value $\sqrt{-g}=r^2\sin\theta\, e^{\frac{3\mu+\nu}{2}}$ given in (10), this is easily found to reduce to the form

$$\frac{\partial p_0}{\partial r}=-\frac{\rho_{00}+p_0}{2}\frac{\partial \nu}{\partial r} \quad (22)$$

which furnishes us with a very simple and useful expression for the change in pressure with radius. The equation may be regarded as the general relativity analogue of the Newtonian equation

$$\frac{dp}{dr}=-\rho\frac{d\Psi}{dr}$$

where ρ is now expressed in terms of mass per unit volume, and indeed can be shown to reduce to this in case the gravitational field is weak and the sys-

[6] See Eddington, reference 4, equation (55.6).

tem consists of ordinary matter with the pressure p_0 negligible compared with the density ρ_{00}.

It is also of interest to note that equation (22) can alternatively be derived by combining equations (17), (18) and (19), without the use of the mechanical principle given by equation (21). The mechanical principle and the equality of the two different expressions for pressure thus imply the same restrictions on the pressure distribution within the sphere.

Returning now to the mechanical equation (21) and considering the cases $\sigma = 2$ and $\sigma = 3$, it is easy to show by a similar method to the one just used that we obtain the results

$$\frac{\partial p_0}{\partial \theta} = \frac{\partial p_0}{\partial \phi} = 0 \tag{23}$$

as was to be expected.

Finally, considering the case $\sigma = 4$, we obtain by substitution into (21)

$$\frac{\partial}{\partial t}(\rho_{00}\sqrt{-g}) - \frac{1}{2}\mathfrak{T}^{\alpha\beta}\frac{\partial g_{\alpha\beta}}{\partial t} = 0$$

and since by our hypothesis of a static system the $g_{\alpha\beta}$ are independent of the time t, we have the result

$$\frac{\partial \rho_{00}}{\partial t} = 0 \tag{24}$$

the proper density remaining constant with time at each point in the distribution, in complete agreement with our original assumption of a static system

§5. Mechanical Treatment of Temperature Distribution in the Case of Radiation

In the case of a spherical distribution of pure black-body radiation such as might surround a gravitating sphere of denser matter, relativistic mechanics without a resort to relativistic thermodynamics will be sufficient to determine the temperature distribution. This arises because of the simple relations in the case of black-body radiation directly connecting the thermodynamic quantity temperature with the mechanical quantities energy density and pressure.

For the energy density and pressure of black-body radiation we can evidently write in accordance with well known equations

$$\rho_{00} = aT_0^4 \tag{25}$$

and

$$p_0 = \tfrac{1}{3}aT_0^4 \tag{26}$$

where a is the Stefan-Boltzmann constant and T_0 is the *proper* temperature, as measured by a local observer, located at a point where ρ_{00} and p_0 are the proper macroscopic energy density and proper pressure of the radiation.

Substituting these expressions into our mechanical equation (22), we at once obtain as exact relativistic expressions for the temperature distribution within a field of radiation

$$\frac{d\ ln\ T_0}{dr} = -\frac{1}{2}\frac{d\nu}{dr} \tag{27}$$

or

$$T_0 = Ce^{-\nu/2} \tag{28}$$

where C is a constant of integration. Furthermore, in the case of weak enough fields so that the Newtonian theory of gravitation is a sufficient approximation, equation (27) can be shown to reduce to

$$\frac{d\ ln\ T_0}{dr} = -\frac{1}{c^2}\frac{d\Psi}{dr} = -\frac{g}{c^2} \tag{29}$$

in agreement with equation (8) obtained by our preliminary treatment. The qualitative nature of this result is entirely reasonable since it is evident that the pressure of radiation must increase as we go to lower gravitational levels in order to support the increasing amount of the radiation above, and in the case of pure radiation such an increase in pressure can only be the result of an increase in temperature.

It is a matter of great interest that we have thus been able to determine, by a straightforward application of relativity mechanics without any resort to the new relativistic thermodynamics, the effect of gravity on temperature distribution in the particular case of a field of pure radiation. We have thus obtained in a rather unimpeachable manner a justification in at least one case for our original general idea, as expressed in §1, that the condition of thermodynamic equilibrium under the action of gravitation would involve higher temperatures at lower gravitational levels in order to prevent the downward flow of heat, and shall be ready to expect similar effects of gravitational action on temperature in more complicated cases whose solution will involve our new system of relativistic thermodynamics.

§6. The Thermodynamic Conditions for Equilibrium

To prepare for our thermodynamic treatment, we may now restate the conditions for equilibrium in a static system obtained in the previous development of relativistic thermodynamics.[7] Using the polar coordinates adopted in §4 of this article, these conditions took the form that the general relativity expression for the entropy of the system lying within the spherical shell between the constant radii r_1 to r_2 should be a maximum in accordance with the variational equation

$$\delta\left[4\pi\int_{r_1}^{r_2}\phi_0\, e^{3\mu/2}\, r^2 dr\right] = 0 \tag{30}$$

under the subsidiary condition coming from consideration of the energy-momentum principle

[7] See in particular §5 in the article in This Journal.

$$\delta\mu=\delta\mu'=\delta\nu=\delta\nu'=0 \quad (\text{at } r_1 \text{ and } r_2) \tag{31}$$

where μ and ν are the exponents occurring in our expression for the line element, and the quantity ϕ_0 occurring in equation (30) is the proper density of entropy.

§7. Thermodynamic Treatment of Temperature Distribution in the Case of Radiation

Let us now make use of the thermodynamic method to obtain a treatment of temperature distribution in the case of radiation. To do this we can re-express the entropy density ϕ_0 occurring in equation (30) in terms of energy density ρ_{00}, and by means of our previous relation connecting energy density with the metric can obtain the condition for maximum entropy in a form in which it depends explicitly on the metrical variable μ and its differential coefficients. The variation indicated in equation (30) can then be performed and the subsidiary conditions imposed by equation (31) on the variable μ easily introduced.

For the proper density of entropy ϕ_0 in terms of the proper temperature T_0 we can evidently write in accordance with the well known properties of black-body radiation

$$\phi_0=\frac{4}{3}aT_0^3 \tag{32}$$

where a is the Stefan-Boltzmann constant. Combining this with equation (25), connecting the energy density with temperature, we obtain

$$\phi_0=\frac{4}{3}a^{1/4}\rho_{00}^{3/4} \tag{33}$$

and using equation (19) which connects the energy density with the metric we can write

$$\phi_0=-\frac{4a^{1/4}}{24\pi}e^{-3\mu/4}\left[\mu''+\frac{2\mu'}{r}+\frac{\mu'^2}{4}\right]^{3/4}. \tag{34}$$

Substituting this into equation (30) and dividing out the constant factors, we finally obtain as the condition of maximum entropy in terms of the metrical variable μ

$$\delta\int_{r_1}^{r_2}\left(\mu''+\frac{2\mu'}{r}+\frac{\mu'^2}{4}\right)^{3/4}e^{3\mu/4}\,r^2dr=0 \tag{35}$$

under the condition

$$\delta\mu=\delta\mu'=0 \quad (\text{at } r_1 \text{ and } r_2). \tag{36}$$

Performing the variation indicated in equation (35) we obtain

$$\int_{r_1}^{r_2}\left[\frac{3}{4}\left(\mu''+\frac{2\mu'}{r}+\frac{\mu'^2}{4}\right)^{-1/4}\left(\delta\mu''+\frac{2}{r}\delta\mu'+\frac{\mu'}{2}\delta\mu'\right)e^{3\mu/4}+\frac{3}{4}\left(\mu''+\frac{2\mu'}{r}+\frac{\mu'^2}{4}\right)^{3/4}e^{3\mu/4}\delta\mu\right]r^2\,dr=0 \tag{37}$$

and resubstituting the expression for energy density given by equation (19) this can be rewritten in the simpler form

$$\int_{r_1}^{r_2}\left[\frac{e^{(\mu/2)}r^2}{\rho_{00}{}^{1/4}}\left(\delta\mu''+\frac{2}{r}\delta\mu'+\frac{\mu'}{2}\delta\mu'\right)-8\pi\rho_{00}{}^{3/4}\,e^{3\mu/2}\,r^2\,\delta\mu\right]dr=0$$

Noting, however, in accordance with equation (36) that $\delta\mu'$ and $\delta\mu$ are equal to zero at the limits r_1 and r_2 this can evidently be transformed in the usual manner with the help of partial integrations, dropping terms that become zero at the limits, to the following form containing $\delta\mu$ alone.

$$\int_{r_1}^{r_2}\left[\frac{d^2}{dr^2}\left(\frac{e^{\mu/2}r^2}{\rho_{00}{}^{1/4}}\right)-2\frac{d}{dr}\left(\frac{e^{\mu/2}r}{\rho_{00}{}^{1/4}}\right)-\frac{d}{dr}\left(\frac{e^{\mu/2}r^2}{\rho_{00}{}^{1/4}}\,\frac{\mu'}{2}\right)-8\pi\rho_{00}{}^{3/4}\,e^{3\mu/2}\,r^2\right]\delta\mu dr=0. \quad (38)$$

This equation, however, can be true for arbitrary variations $\delta\mu$ only if the quantity in the square brackets is equal to zero, and this can evidently be rewritten to give us

$$\frac{d}{dr}\left\{e^{\mu/2}\,r^2\,\frac{d}{dr}\left(\frac{1}{\rho_{00}{}^{1/4}}\right)\right\}=8\pi\rho_{00}{}^{3/4}\,e^{3\mu/2}\,r^2. \quad (39)$$

And substituting the relation betwen energy density ρ_{00} and temperature T_0 given by equation (25), this becomes

$$\frac{d}{dr}\left\{e^{\mu/2}\,r^2\,\frac{d}{dr}\left(\frac{1}{T_0}\right)\right\}=8\pi\,\frac{\rho_{00}}{T_0}\,e^{3\mu/2}\,r^2. \quad (40)$$

To solve this equation for T_0 as a function of r, we note that in the case of radiation we have $8\pi\rho_{00}=4\pi(\rho_{00}+3p_0)$ and substituting equation (20) we can then rewrite (40) in the form

$$\frac{d}{dr}\left\{e^{\mu/2}\,r^2\,\frac{d}{dr}\left(\frac{1}{T_0}\right)\right\}=\frac{e^{-\nu/2}}{T_0}\,\frac{d}{dr}\left\{e^{\mu/2}\,r^2\,\frac{d}{dr}(e^{\nu/2})\right\}$$

or

$$\left(\frac{1}{T_0}\right)^{-1}\frac{d}{dr}\left\{e^{\mu/2}\,r^2\,\frac{d}{dr}\left(\frac{1}{T_0}\right)\right\}=(e^{\nu/2})^{-1}\,\frac{d}{dr}\left\{e^{\mu/2}\,r^2\,\frac{d}{dr}(e^{\nu/2})\right\}. \quad (41)$$

Postponing a more general discussion of the solution of this equation until the next section, §8, where the equation again occurs, we note at once that a particular solution of the equation is given by

$$T_0=Ce^{-\nu/2} \quad (42)$$

where C is a constant of integration and this equation for the temperature distribution in a field of radiation which has come to equilibrium under the action of gravity is exactly the same as equation (28) which we obtained in §5. Hence in this simple case of radiation, where a mechanical treatment can be given, the thermodynamic and the mechanical treatment of temperature

distribution under the action of gravity lead to the same result. This can be regarded as some confirmation of the validity of the system of relativistic thermodynamics which I have proposed.

§8. Temperature Distribution in the General Case of Any Perfect Fluid

Let us now consider the application of our condition for a maximum of the relativistic expression for entropy

$$\delta\left[4\pi\int_{r_1}^{r_2}\phi_0\, e^{3\mu/2} r^2 dr\right]=0 \tag{43}$$

to a determination of the temperature distribution in the general case of any perfect fluid. To apply this equation it will be convenient to note that $4\pi e^{3\mu/2} r^2\, dr$ is evidently the *proper* spatial volume lying in the spherical shell between r and $r+dr$. This can be seen from the general relation for the element of proper spatial volume

$$dV_0\, ds = \sqrt{-g}\, dx_1 dx_2 dx_3 dx_4$$

which, in the case of our system and line element (9), gives

$$dV_0 = e^{\frac{3\mu+\nu}{2}} r^2 \sin\theta dr d\theta d\phi \frac{dt}{ds} = e^{3\mu/2} r^2 \sin\theta dr d\theta d\phi.$$

And if we integrate this over all values of θ and ϕ, we obtain

$$V_0 = 4\pi e^{3\mu/2} r^2\, dr \tag{44}$$

for the proper spatial volume lying between r and $r+dr$, where V_0 is of course an infinitesimal quantity.

Under these circumstances, since ϕ_0 is the proper density of entropy, we may evidently write

$$S_0 = 4\pi\, \phi_0\, e^{3\mu/2} r^2\, dr \tag{45}$$

as an expression for the entropy, as measured in proper coordinates, associated with the material lying between r and $r+dr$. As this quantity of entropy is measured in proper coordinates, it will evidently obey the classical laws of thermodynamics and may be taken as a function of temperature T_0, volume V_0 and number of molecules $N_1, N_2 \cdots N_n$ of the n different components which are necessary to specify the composition, in the way ordinarily employed in thermodynamics.

We are now ready to investigate the temperature distribution in our fluid. To do this let us consider the effect of a variation in the temperature T_0 and volume V_0 associated with the shell r to $r+dr$, keeping the composition of the material in this shell unaltered, that is holding $N_1 \cdots N_n$ constant. Under these conditions, we shall have in accordance with the principles of ordinary thermodynamics

$$\delta S_0 = \frac{\delta U_0}{T_0} + \frac{p_0}{T_0}\delta V_0 \tag{46}$$

and in accordance with equations (44) and (45) this can evidently be written in the form

$$\delta(4\pi\,\phi_0\, e^{3\mu/2}\, r^2\, dr) = \frac{\delta(4\pi\,\rho_{00}\, e^{3\mu/2}\, r^2\, dr)}{T_0} + \frac{p_0}{T_0}\,\delta(4\pi\, e^{3\mu/2}\, r^2\, dr). \tag{47}$$

Substituting this in equation (43) for the maximum of the relativistic expression for entropy we now obtain

$$4\pi \int_{r_1}^{r_2} \left[\frac{\delta(\rho_{00}\, e^{3\mu/2})}{T_0} + \frac{p_0}{T_0}\,\delta(e^{3\mu/2})\right] r^2 dr = 0 \tag{48}$$

which gives the condition for a maximum of the relativistic entropy in a form which can be made to depend solely on the variation of the metrical variable μ and its derivatives, by substituting for the energy density ρ_{00} its values as given by equation (19). Doing so we obtain

$$\int_{r_1}^{r_2} \left[-\frac{1}{2T_0}\delta\left\{e^{\mu/2}\left(\mu'' + \frac{2\mu'}{r} + \frac{\mu'^2}{4}\right)\right\} + \frac{4\pi p_0}{T_0}\,\delta(e^{3\mu/2})\right] r^2 dr = 0 \tag{49}$$

Performing the indicated variations, we have

$$\int_{r_1}^{r_2} \left[-\frac{e^{\mu/2}}{2T_0}\left(\delta\mu'' + \frac{2\delta\mu'}{r} + \frac{\mu'}{2}\,\delta\mu'\right) - \frac{e^{\mu/2}}{4T_0}\left(\mu'' + \frac{2\mu'}{r} + \frac{\mu'^2}{4}\right)\delta\mu + \frac{12\pi p_0}{2T_0}\, e^{3\mu/2}\,\delta\mu\right] r^2 dr = 0.$$

Noting, however, that the variations are to be carried out in accordance with equation (31) which gives $\delta\mu' = \delta\mu = 0$ at r_1 and r_2, the first term in the integrand can evidently be transformed in the usual manner with the help of partial integrations, dropping terms that become zero at the limits, to a form depending on $\delta\mu$ alone; and the second term in the integrand can be simplified by resubstituting equation (19) for the energy density ρ_{00}. We thus obtain

$$\int_{r_1}^{r_2} \left[\frac{d^2}{dr^2}\left(\frac{e^{\mu/2}\, r^2}{T_0}\right) - 2\frac{d}{dr}\left(\frac{e^{\mu/2}\, r}{T_0}\right) - \frac{d}{dr}\left(\frac{e^{\mu/2}\, r^2}{T_0}\,\frac{\mu'}{2}\right) - \frac{4\pi(\rho_{00} + 3p_0)}{T_0}\, e^{3\mu/2}\, r^2\right] \delta\mu\, dr = 0.$$

This equation can be true, however, for arbitrary variations $\delta\mu$ only if the term in square brackets is equal to zero, and this can evidently be rewritten to give us

$$\frac{d}{dr}\left\{e^{\mu/2}\, r^2 \frac{d}{dr}\left(\frac{1}{T_0}\right)\right\} = \frac{4\pi(\rho_{00} + 3p_0)}{T_0}\, e^{3\mu/2}\, r^2 \tag{50}$$

and substituting equation (20), we finally obtain as an expression connecting T_0 with the coordinate r and the metrical variables μ and ν

$$\frac{d}{dr}\left\{e^{\mu/2}r^2\frac{d}{dr}\left(\frac{1}{T_0}\right)\right\} = \frac{e^{-\nu/2}}{T_0}\frac{d}{dr}\left\{e^{\mu/2}r^2\frac{d}{dr}(e^{\nu/2})\right\}. \tag{51}$$

This differential equation for T_0 is the same as equation (41) which we got when we applied the thermodynamic method to pure radiation. A first integral for this equation can be written in the form

$$\frac{d\ ln\ T_0}{dr} = -\frac{1}{2}\frac{d\nu}{dr} + \frac{Be^{-\frac{\mu+\nu}{2}}}{r^2}T_0 \tag{52}$$

where B is a constant of integration, and substituting equation (22) this can be written as

$$\frac{d\ ln\ T_0}{dr} = \frac{1}{\rho_{00}+p_0}\frac{dp_0}{dr} + \frac{Be^{-\frac{\mu+\nu}{2}}}{r^2}T_0.$$

If, however, we now assume on physical grounds that at the center of the sphere $r=0$, we have dT_0/dr and dp_0/dr equal to zero, T_0 not equal to zero and the other functions of r finite, it is evident that the constant of integration B must be equal to zero.[8] Under these circumstances the second integral of our equation is then easily seen to be

$$T_0 = Ce^{-\nu/2} \tag{53}$$

where C is a second constant of integration.

This result is exactly of the same form as that obtained for radiation alone and that is a satisfactory outcome since our method of derivation did not involve the assumption that any matter at all was necessarily present. The equation gives a definite relation connecting the equilibrium temperature in a gravitational field with the variable ν which is itself determined in a known way by the gravitational field. The general nature of the result can perhaps be more easily appreciated by redifferentiating equation (53) with respect to r and substituting equation (22). We then obtain

$$\frac{d\ ln\ T_0}{dr} = -\frac{1}{2}\frac{d\nu}{dr} = \frac{1}{\rho_{00}+p_0}\frac{dp_0}{dr} \tag{54}$$

and can at once see that temperature and pressure will increase together as we go towards the center of the sphere. It is also of interest to note once more the approximation

$$\frac{d\ ln\ T_0}{dr} = -\frac{1}{c^2}\frac{d\Psi}{dr} = -\frac{g}{c^2}$$

[8] It would be interesting to investigate the possibility of solutions of physical interest with $B \neq 0$.

valid in weak enough fields so that the Newtonian method is applicable, and this is the same equation as was obtained in our preliminary non-rigorous treatment.[9]

§9. The Distribution of Matter in a Sphere of Perfect Fluid

The principles of relativistic thermodynamics which we have used in the preceding section should be sufficient to give us information not only as to the temperature distribution in a sphere of fluid but also as to the equilibrium distribution of matter. To obtain such information let us return once more to our condition for a maximum of the relativistic expression for entropy

$$\delta\left[4\pi\int_{r_1}^{r_2}\phi_0\, e^{3\mu/2}\, r^2\, dr\right]=0. \tag{55}$$

In using this equation to determine the distribution of temperature, we considered the result of varying the temperature as a function of r, holding constant the number of molecules $N_1 \cdots N_n$ of each of the different components of the system in each spherical shell lying between r and $r+dr$. To determine the distribution of matter, on the other hand, we may hold the temperature constant and consider the result of varying the composition of the layers. As simple illustrations, we shall apply this method to a system consisting of a mixture of a perfect monatomic gas and radiation, both on the assumption that radiation and matter are interconvertible, and on the assumption that the total number of molecules in the system cannot be varied.

For the proper density of entropy of a mixture of perfect monatomic gas and radiation, we may evidently write in accordance with well known equations

$$\phi_0=N_0 k\, ln\frac{CT_0^{3/2}}{N_0}+\frac{4}{3}aT_0^3 \tag{56}$$

where N_0 is the number of molecules in unit volume as measured in proper coordinates by a local observer, T_0 is the proper temperature, k and a are respectively the Boltzmann constant and Stefan constant, and C is a constant so chosen that the starting points for the measurement of the entropy of matter and radiation will be in agreement.

If now we vary the proper concentration of molecules N_0 holding the temperature T_0 constant, we obtain

$$\delta\phi_0=\left(k\, ln\frac{CT_0^{3/2}}{N_0}-k\right)\delta N_0. \tag{57}$$

On the other hand for the proper density of energy we evidently have

$$\rho_{00}=N_0mc^2+\tfrac{3}{2}N_0kT_0+aT_0^4 \tag{58}$$

[9] As a justification for the results of this section, my colleague Dr. J. Robert Oppenheimer has kindly pointed out to me that the relation which I have obtained between temperature and gravitational potential is a necessary one if the Planck radiation law is to hold at different gravitational levels.

where m is the rest mass of one molecule and c the velocity of light,—mc^2 thus being the internal energy and $(3/2)kT_0$ the average kinetic energy per molecule. Hence, holding the temperature constant as before, and varying N_0 we obtain

$$\delta\rho_{00}=(mc^2+\tfrac{3}{2}kT_0)\delta N_0 \tag{59}$$

and by combining equations (57) and (59) we can express the variation in the density of entropy in terms of the variation in density of energy in the form

$$\delta\phi_0=\frac{k\ ln\ CT_0^{3/2}/N_0 - k}{mc^2 + 3/2kT_0}\,\delta\rho_{00}$$

or

$$\delta\phi_0 = f(N_0, T_0)\,\delta\rho_{00} \tag{60}$$

where for simplification we have written $f(N_0, T_0)$ as an abbreviation for the coefficient of $\delta\rho_{00}$.

Since $\delta\rho_{00}$, however, can be expressed as a function of the metrical variable μ, we can now return to our equation (55) for maximum entropy and write as a condition for equilibrium

$$4\pi\int_{r_1}^{r_2}\left[\delta\phi_0\, e^{3\mu/2} + \tfrac{3}{2}\phi_0\, e^{3\mu/2}\,\delta\mu\right] r^2dr=0$$

or substituting equation (60)

$$4\pi\int_{r_1}^{r_2}\left[f(N_0,T_0)e^{3\mu/2}\,\delta\rho_{00} + \tfrac{3}{2}\phi_0\, e^{3\mu/2}\,\delta\mu\right] r^2dr=0 \tag{61}$$

and substituting in turn the value of ρ_{00} in terms of the metrical variable give by equation (19) we obtain

$$\int_{r_1}^{r_2}\left[-\frac{1}{2}f(N_0,T_0)e^{\mu/2}\left(\delta\mu''+\frac{2}{r}\delta\mu'+\frac{\mu'}{2}\delta\mu'\right)\right.$$
$$\left.+\frac{1}{2}f(N_0,T_0)e^{\mu/2}\left(\mu''+\frac{2\mu'}{r}+\frac{\mu'^2}{4}\right)\delta\mu + 4\pi\frac{3}{2}\phi_0\, e^{3\mu/2}\,\delta\mu\right] r^2dr=0.$$

Noting as in previous sections, however, that the variations are to be carried out in accordance with equation (31) which gives $\delta\mu'=\delta\mu=0$ at r_1 and r_2, the first term in the integrand can evidently be transformed in the usual manner with the help of partial integrations, dropping terms that become zero at the limits, to a form depending on $\delta\mu$ alone; and the second term in the integrand can be simplified by resubstituting equation (19) for the energy density ρ_{00}. We thus obtain

$$\int_{r_1}^{r_2}\left[\frac{d^2}{dr^2}\{f(N_0,T_0)e^{\mu/2}r^2\} - 2\frac{d}{dr}\{f(N_0,T_0)e^{\mu/2}\,r\}\right.$$
$$\left.-\frac{d}{dr}\left\{f(N_0,T_0)e^{\mu/2}\,r^2\,\frac{\mu'}{2}\right\} + 4\pi\{2f(N_0,T_0)\rho_{00}-3\phi_0\}\,e^{3\mu/2}\,r^2\right]\delta\mu dr = 0$$

and combining the first three terms this can be rewritten in the form

$$\int_{r_1}^{r_2}\left[\frac{d}{dr}\left\{e^{\mu/2}r^2\frac{d}{dr}f(N_0,T_0)\right\}+4\pi\left\{2f(N_0,T_0)\rho_{00}-3\phi_0\right\}e^{3\mu/2}r^2\right]\delta\mu dr=0. \quad (62)$$

This equation has resulted from an application of the condition for maximum relativistic entropy under the subsidiary condition, given by equation (31), which satisfies the requirements of the energy-momentum principle. In case we assume the ready interconvertibility of matter and radiation no further subsidiary conditions need be introduced. On the other hand, if we are interested in what might be only a temporary condition of equilibrium reached in a length of time such that the total number of molecules could not change, we must evidently add as a further subsidiary condition

$$\delta\left[4\pi\int_{r_1}^{r_2}N_0\,e^{3\mu/2}r^2\,dr\right]=0 \quad (63)$$

where N_0 is the proper concentration of molecules and as we saw above $4\pi\,e^{3\mu/2}r^2dr$ is the proper volume in the spherical shell lying between r and $r+dr$.

Performing the indicated variation, keeping of course the temperature constant as in the previous variation, and substituting the value for δN_0 given by equation (58), we obtain

$$4\pi\int_{r_1}^{r_2}\left[\frac{e^{3\mu/2}}{mc^2+(3/2)kT_0}\delta\rho_{00}+\frac{3}{2}N_0\,e^{3\mu/2}\,\delta\mu\right]r^2dr=0.$$

This equation, however, is of the same general form as (61) above, and can be treated by the same methods which led from (61) to (62), and will then evidently reduce to

$$\int_{r_1}^{r_2}\left[\frac{d}{dr}\left\{e^{\mu/2}r^2\frac{d}{dr}\left(\frac{1}{mc^2+(3/2)kT_0}\right)\right\}+4\pi\left\{\frac{2\rho_{00}}{mc^2+(3/2)kT_0}-3N_0\right\}e^{3\mu/2}r^2\right]\delta\mu dr=0. \quad (64)$$

Equations (64) and (62) may now be combined by the method of Lagrange to give us a single condition

$$\int_{r_1}^{r_2}\left[\frac{d}{dr}\left\{e^{\mu/2}r^2\frac{d}{dr}\left(f(N_0,T_0)+\frac{\lambda}{mc^2+(3/2)kT_0}\right)\right\}+4\pi\left\{2\left(f(N_0,T_0)+\frac{\lambda}{mc^2+(3/2)kT_0}\right)\rho_{00}-3\phi_0-3\lambda N_0\right\}e^{3\mu/2}r^2\right]\delta\mu dr=0$$

where λ is a constant undetermined multiplier, whose value will be zero in case equilibrium between matter and radiation is established, since the additional condition (63) will then not be needed. This equation, however, can only be true for arbitrary variations $\delta\mu$, if the quantity in square brackets

is equal to zero. Hence, resubstituting the value of $f(N_0, T_0)$ given by equation (60) we have as our final differential equation

$$\frac{d}{dr}\left\{e^{\mu/2}r^2\frac{d}{dr}\frac{k\ ln\ CT_0^{3/2}/N_0-k+\lambda}{mc^2+(3/2)kT_0}\right\}$$
$$=4\pi\left\{3\phi_0+3\lambda N_0-2\frac{k\ ln\ CT_0^{3/2}/N_0-k+\lambda}{mc^2+(3/2)kT_0}\rho_{00}\right\}e^{3\mu/2}r^2 \quad (65)$$

where $\lambda=0$ in case the equilibrium between matter and radiation is established.

We have thus obtained a second order differential equation connecting the thermodynamic quantities concentration N_0 and temperature T_0 with the coordinate r. We have already found in the previous section, §8, however, equations for T_0 as a function of r, and hence the present equation requires that N_0 be such a function of T_0 as not to disagree with the previous results. We shall then suggest as an expression for the dependence of N_0 on T_0 and hence implicitly on r

$$k\ ln\frac{CT_0^{3/2}}{N_0}-k+\lambda=\frac{mc^2}{T_0}+\frac{3}{2}k \quad (66)$$

or

$$N_0=Ce^{\lambda/k-5/2}T_0^{3/2}e^{-mc^2/kT_0}$$

and test the suggestion by substituting into (65). Doing so, we obtain

$$\frac{d}{dr}\left\{e^{\mu/2}r^2\frac{d}{dr}\left(\frac{1}{T_0}\right)\right\}=4\pi\left\{3\phi_0+3\lambda N_0-\frac{2\rho_{00}}{T_0}\right\}e^{3\mu/2}r^2.$$

Comparing the first form of equation (66), however, with the expression for ϕ_0 given by (56), and introducing the expression for ρ_{00} given by (58), we obtain

$$\frac{d}{dr}\left\{e^{\mu/2}r^2\frac{d}{dr}\left(\frac{1}{T_0}\right)\right\}=4\pi\left\{\frac{3N_0mc^2}{T_0}+\frac{15}{2}N_0k-3\lambda N_0+4aT_0^3\right.$$
$$\left.+3\lambda N_0-2\frac{N_0mc^2}{T_0}-3N_0k-2aT_0^3\right\}e^{3\mu/2}r^2$$
$$=4\pi\left\{\frac{N_0mc^2+(3/2)N_0kT_0+aT_0^4+3(N_0kT_0+(a/3)T_0^4)}{T_0}\right\}e^{3\mu/2}r^2$$
$$=4\pi\frac{(\rho_{00}+3p_0)}{T_0}e^{3\mu/2}r^2 \quad (67)$$

since the gas pressure is evidently N_0kT_0 and the radiation pressure $\frac{1}{3}aT_0^4$. And this equation is exactly the same as our general equation (50) for the dependence of temperature on the coordinate and metric as obtained in the previous section §8. Hence our suggested expression equation (66) for the dependence of the concentration on temperature can be accepted as

satisfying the information previously obtained as to the dependence of temperature on the metric, and thus as a satisfactory solution of the problem of the distribution of a perfect monatomic gas in a gravitational field.

It is also significant to point out that equation (66) can be subjected to another test, since this expression for the proper concentration of the gas makes it possible to calculate the partial pressure of the gas and by combining with the partial pressure of radiation, then examine the dependence of total pressure on the radius r to see if it agrees with the purely mechanical equation $dp_0/dr = -(\rho_{00}+p_0)\nu'/2$, obtained in §4. And as a matter of fact equation (66) does lead to this result.[10]

Finally, it is interesting to compare the dependence of proper concentration on proper temperature given by equation (66) with the result obtained for the equilibrium concentration in flat space-time by Stern[11] and myself.[12] Taking the case where equilibrium between matter and radiation has been established, we have $\lambda = 0$ and equation (66) can be written

$$N_0 = (Ce^{5/2})\, T_0^{3/2}\, e^{-mc^2/kT_0}$$

which agrees with my previous result as it stands, and agrees with the Stern result if we assign to the constant term $(Ce^{5/2})$ the not necessarily correct value which Stern obtained for it. Hence the conclusion can again be stated, owing to the great magnitude of the negative exponent for reasonable values of m and T, that the equilibrium concentration would be extremely small unless the constant term could be shown to have an enormous magnitude.

§10. Conclusion

In accordance with the special theory of relativity and the equivalence principle all forms of energy, including heat, must be regarded as having both inertia and weight, and the purpose of the present article has been to investigate, in as consequent a manner as may be, the thermodynamic implications of the notion that heat has weight. The most striking result of the investigation has been the discovery of a definite relation connecting gravitational potential with the distribution of temperature throughout a system which has come to thermodynamic equilibrium.

Qualitatively, the increase in equilibrium temperature which was found to accompany decrease in gravitational potential, may be regarded as due to the necessity of having a temperature gradient to prevent the flow of heat from places of higher to those of lower potential energy; and quantitatively, a first approximation to the magnitude of this temperature gradient was

[10] It may seem strange that this purely mechanical equation holding within the interior of the system should be derivable from the application of thermodynamics to the system as a whole. The result, however, is the relativity analogue to the equation for change in pressure with height obtained by Gibbs ("Scientific Papers," Longmans, Green 1906, equation 230, p. 145) in his thermodynamic treatment of the conditions of equilibrium under the influence of gravity. Indeed the whole treatment of this article may be regarded as the relativistic extension of this part of Gibbs' work.

[11] Stern, Zeits. f. Elektrochem. **31**, 448 (1925); Trans. Farad. Soc. **21**, 477 (1925–26).

[12] Tolman, Proc. Nat. Acad. **12**, 670 (1926).

obtained by modifying the classical thermodynamics merely by ascribing to each given intrinsic quantity of energy the right additional quantity of potential gravitational energy. For a rigorous treatment, however, it was obviously necessary to investigate the whole problem from the standpoint of general relativity, and this was done using the extension of thermodynamics to general relativity which I have previously given. In this way it was possible to obtain what appears to be a rigorous equation connecting equilibrium temperature with gravitational potential. In addition in the case of black-body radiation it was possible to test the thermodynamic method, since the same temperature distribution in the case of this simple system was also obtained by the use of relativistic mechanics, without the necessity for the use of the new relativistic thermodynamics.

This discovery of a dependence of equilibrium temperature on gravitational potential must be regarded as something essentially new in thermodynamics, since uniform temperature throughout any system which has come to equilibrium has hitherto been taken as an inescapable part of thermodynamic theory. The new result hence has a very considerable theoretical interest, and even though the effect of gravitational potential on temperature may usually be extremely small the result may sometime be of experimental or observational interest.

THE DETERMINATION OF ELECTRON DISTRIBUTIONS FROM MEASUREMENTS OF SCATTERED X-RAYS

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Abstract

A calculation based on classical electromagnetic theory is made of the intensity of the x-rays scattered by an atom in which the electrons are arranged with random orientation and with arbitrary radial distribution. Conversely *an expression is derived for the radial distribution of the electrons in an atom*, assuming that they have random orientation. This expression has the form of a Fourier integral, which can be evaluated from observed intensities of the scattered x-rays for different wave-lengths and angles.

A comparison of this calculation with Wentzel's quantum theory of x-ray scattering suggests the introduction of a certain correction factor to express more nearly the intensity of the modified rays. It is also noted that the interpretation of $\psi\bar{\psi}$ *as a probability of the occurrence of an electron* leads to the correct value for the intensity of total scattered x-rays.

As an example of the application of the new method of calculation, Barrett's experimental data for the scattering of x-rays by helium are analyzed to give *the distribution of the electrons in the helium atom*. The resulting distribution is in close agreement with the value calculated by Pauling on the basis of wave mechanics, but differs by more than the probable experimental error from the electron orbits given by Bohr's theory.

1. Introduction

IT IS well known that the intensity of the x-rays scattered at small angles may be considerably greater than is anticipated on the assumption that each electron in the scattering material acts independently of the other electrons. When the scattering of x-rays by solids and liquids is considered, at least a part of this "excess scattering" may be ascribed to the interference between the rays scattered by neighboring atoms. In the case of gases, however, such interference is negligible, since the phases of the rays scattered by neighboring molecules are random. It has nevertheless long been recognized[1] that groupings of the electrons in the atoms themselves should result in some excess scattering in the forward direction. Calculations of the intensity of the scattered x-rays for typical electron distributions have in fact been made by Debye,[2] Schott,[3] the writer,[4] Glocker[5] and others. The converse problem of determining the electron distribution corresponding to an observed angular

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[2] P. Debye, Ann. d. Physik **46**, 809 (1915).
[3] G. A. Schott, Proc. Roy. Soc. **96**, 695 (1920).
[4] A. H. Compton, Washington University Studies, **8**, 98 (1921).
[5] R. Glocker, Zeits. f. Physik **5**, 54 (1921).

distribution of scattered x-rays has not however been attempted. We shall in the present paper obtain a solution of this problem which applies to certain important cases, and illustrate its application by determining the electron distribution in atoms of helium.

Because of the very important information which can thus be obtained regarding atomic structures, the problem would doubtless have been long ago pressed to a solution had it not been for an obstinate theoretical difficulty. Calculations of the effect of interference on the intensity of x-ray scattering are based upon the classical electron theory and electrodynamics. In the course of these x-ray diffraction studies, however, it became evident[6] that these classical theories are inadequate to supply a complete solution of the problem of the intensity of scattered rays. The problem was accordingly "laid on the table" until a new quantum dynamics should be developed which would be able to supply a more reliable solution. Recently Wentzel[7] has shown how the wave mechanics may be applied to this problem, and from his discussion it appears that the classical electron theory itself should give results which are not greatly in error.

In the meantime, closely allied problems have been successfully attacked on the basis of classical electron theory. In our studies of the diffraction of x-rays by crystals, which is of course only a special case of the general problem of x-ray scattering, application of the usual wave theory has enabled us to arrive at satisfactory arrangements of the atoms in the crystals, and has recently been used to determine also electron distributions in the atoms.[8] We have every reason to believe that the information supplied by this work regarding atomic arrangements is reliable, and even the electron distributions found by its use are too satisfactory to admit any major error in the method of analysis. Similarly the classical wave diffraction theory has been successfully applied to the x-ray study of molecular shapes and sizes of liquids,[9] and very recently also to the study of interatomic distances in gaseous molecules.[10] We are thus encouraged to undertake again a more detailed analysis of the scattering of x-rays by gases, on the basis of classical theory. The results of this analysis will then be compared with Wentzel's conclusions, to see what modifications are necessary in light of quantum mechanics.

2. Intensity of the X-rays Scattered by a Group of Electrons having a Random Angular Distribution

Let us suppose that an atom has Z electrons whose distances from the nucleus are at any instant r_1, $r_2 \cdots r_s$, and whose angular distribution is random. We imagine that this atom is traversed by an x-ray wave propagated

[6] A. H. Compton, Bull. Nat. Res. Council No. 20, p. 10 (1922).

[7] G. Wentzel, Zeits. f. Physik **43,** 1 and 779 (1927).

[8] For summaries of the latter work, *cf, e.g.*, A. H. Compton, "X-rays and Electrons," Chapter V, or W. L. Bragg, "Electrons et Photons," report of the Fifth Solvay Congress, Paris (1928).

[9] For a summary of this work, *cf. e.g.*, G. W. Stewart, Phys. Rev. Supp., Jan., 1930.

[10] P. Debye, L. Bewilogua and F. Ehrhardt, Phys. Zeits. **30,** 84 (1929); Ber. Sächsischen Ak. d. Wiss. zu Leipzig **81,** 29 (1929).

along the X axis, and that the forced oscillations of the electrons give rise to a scattered wave at an arbitrary distant point P at an angle ϕ. If A_e is the amplitude of the electric vector and δ the phase at P of the wave scattered by an electron coincident with the nucleus, the electric vector due to the n^{th} electron in the group is (Fig. 1),

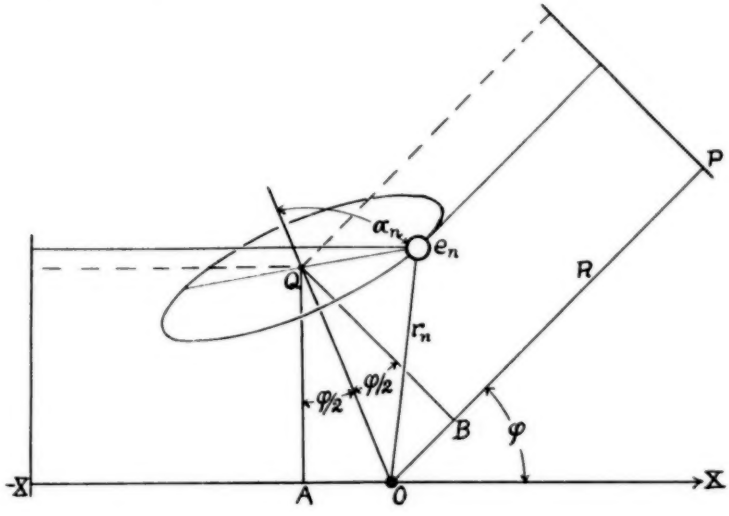

Fig. 1.

$$E_n = A_e \cos \{\delta - (2\pi/\lambda) 2r_n \cos \alpha_n \sin (\phi/2)\}, \tag{1}$$

where $2r_n \cos \alpha_n \sin (\phi/2)$ is the total difference in path[11] between the ray scattered from e_n and that scattered from O, and α_n is the angle between Oe_n and the line OQ which bisects the angle $-XOP$. Equation (1) may be written

$$E_n = A_e \cos (\delta - x_n), \tag{2}$$

where

$$x_n = (4\pi r_n/\lambda) \cos \alpha_n \sin (\phi/2). \tag{3}$$

The total electric vector due to all the electrons in the atomic group is then,

$$E = \sum_1^Z E_n = A_e \sum_1^Z \cos (\delta - x_n). \tag{4}$$

Let us choose the origin of time such that the phase of the wave scattered from O is $\delta = pt$, where $p = 2\pi\nu$ is the phase frequency of the incident wave. The electric vector at the instant t is then, from Eq. (4),

$$E = A_e \sum_1^Z \cos (pt - x_n)$$

$$= A_e \sum_1^Z (\cos pt \cos x_n + \sin pt \sin x_n). \tag{5}$$

[11] Cf. e.g., A. H. Compton, "X-rays and Electrons," p. 385.

The intensity of the scattered ray at this instant is however proportional to E^2, say bE^2, or,

$$I_i = bA_e^2\left\{\sum_1^Z(\cos pt\cos x_n + \sin pt\sin x_n)\right\}^2. \tag{6}$$

When this expression is averaged over a complete cycle, from $t=0$ to $t=2\pi/p$, all the terms in the summation disappear except those of the form

$$\cos x_m\cos x_n + \sin x_m\sin x_n,$$

and we find for the intensity averaged over a cycle,

$$I_a = \frac{1}{2}bA_e^2\sum_1^Z{}_m\sum_1^Z{}_n(\cos x_m\cos x_n + \sin x_m\sin x_n). \tag{7}$$

For a single electron, this becomes

$$I_e = \tfrac{1}{2}bA_e^2. \tag{8}$$

As Thomson has shown,[12] for unpolarized x-rays

$$I_e = \frac{Ie^4}{2m^2R^2c^4}(1+\cos^2\phi), \tag{9}$$

where I is the intensity of the primary beam traversing the electron, e, m and c have their usual significance, and R is the distance from O to P. Equation (7) may thus be written,

$$I_a = I_e\sum_1^Z\sum_1^Z(\cos x_m\cos x_n + \sin x_m\sin x_n). \tag{10}$$

Since we have assumed that the electrons have random angular distribution, we must now average this intensity over all angles α_n. The probability that any α will lie between α and $\alpha+d\alpha$ is for random orientation $\frac{1}{2}\sin\alpha\,d\alpha$. Writing then

$$x_n = z_n\cos\alpha_n, \tag{11}$$

where

$$z_n \equiv (4\pi r_n/\lambda)\sin(\phi/2), \tag{12}$$

the probable contribution to the intensity due to the orientations α_n is

$$\begin{aligned} dI_a = I_e\Bigg\{ &\sum_1^Z\sum_1^Z{}_{m\neq n}\tfrac{1}{4}[\cos(z_m\cos\alpha_m)\cos(z_n\cos\alpha_n) \\ &+ \sin(z_m\cos\alpha_m)\sin(z_n\cos\alpha_n)]\times\sin\alpha_m\sin\alpha_n d\alpha_m d\alpha_n \\ &+ \sum_1^Z\tfrac{1}{2}[\cos^2(z_n\cos\alpha_n)+\sin^2(z_n\cos\alpha_n)]\sin\alpha_n d\alpha_n\Bigg\}. \end{aligned}$$

[12] J. J. Thomson, Conduction of Electricity through Gases, 2nd Ed., p. 325; or cf. "X-rays and Electrons," p. 60.

Integrating over all values of α_m and α_n this takes the simple form,

$$I_r = I_e\left\{Z + \sum_1^Z \sum_1^Z{}_{m\neq n} \frac{\sin z_m}{z_m} \frac{\sin z_n}{z_n}\right\}. \tag{13}$$

Equation (13) represents the scattering by electrons arranged at fixed distances $r_1, r_2 \cdots$ from the nucleus, but with random orientations.

As an example of the application of this formula, consider the case of an atom with two electrons, both at a distance $r=a$ from the center, but with random orientations. We may write equation (13) in the form

$$S \equiv \frac{I_r}{ZI_e} = 1 + \frac{1}{Z}\sum\sum_{m\neq n} \frac{\sin z_m \sin z_n}{z_m z_n}, \tag{14}$$

which in the present case becomes,

$$S = 1 + \left(\frac{\sin z_a}{z_a}\right)^2. \tag{15}$$

A graph of this expression is shown in Fig. 2 by the solid line. This may be compared with scattering by two electrons separated by a fixed distance $2a$, which is given by the expression[13]

$$S = 1 + \frac{\sin 2z_a}{2z_a}, \tag{16}$$

and is represented in the figure by the broken line.

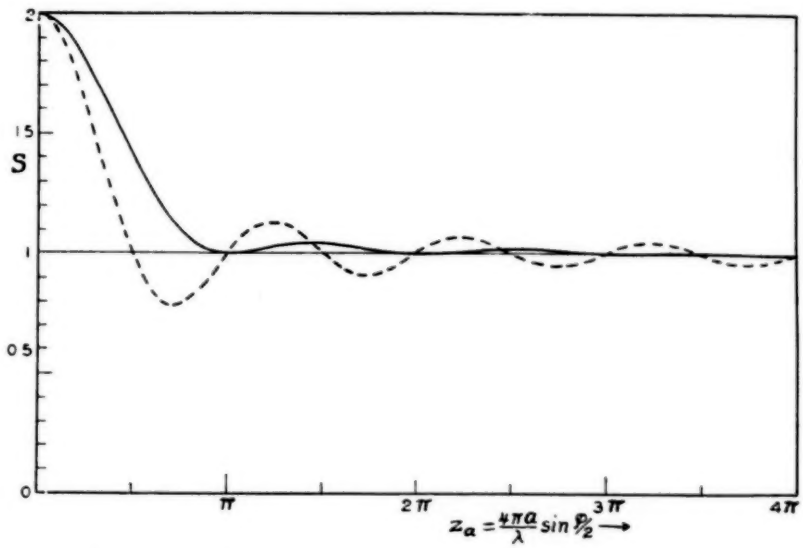

Fig. 2. Relative scattering per electron for an atom of two electrons. Solid line, both electrons at radius a and random orientation. Broken line, electrons at opposite ends of diameter $2a$.

[13] P. Debye, reference 2, or "X-rays and Electrons," p. 72.

If the probability that any one electron shall lie between r and $r+dr$ is $u(r)dr$, and if this probability is the same for every electron, we have,

$$dI_s = I_e\left\{Z + \sum\sum_{m\neq n}\frac{\sin kr_m \sin kr_n}{k^2 r_m r_n}u(r_m)u(r_n)dr_m dr_n\right\},$$

where

$$k \equiv z_m/r_m = (4\pi/\lambda)\sin(\phi/2). \tag{17}$$

Since $u(r_m)$ assumed the same for all electrons, the integral of this expression may be written,

$$I_s = I_e Z + I_e \sum\sum_{m\neq n}\left\{\int_0^a u(r)\frac{\sin kr}{kr}dr\right\}^2,$$

where a is the maximum radius of the atom.
Since

$$\sum_1^Z \sum_1^Z{}_{m\neq n}1 = Z^2 - Z,$$

$$I_s = I_e\left\{Z + (Z^2 - Z)\left[\int_0^a u(r)\frac{\sin kr}{kr}dr\right]^2\right\}. \tag{18}$$

For the relative scattering per electron we thus have

$$S = \frac{I_s}{ZI_e} = 1 + (Z-1)\left\{\int_0^a u(r)\frac{\sin kr}{kr}dr\right\}^2. \tag{19}$$

Expressions (13) or (18) may be applied to calculate the intensity of the rays scattered by an electron group, according as the electrons are at fixed distances from the center of the atom, or as they have a continuous radial distribution.

According to equation (18), I_s should never fall below ZI_e, since the term representing the interference is always positive. In this respect our calculation differs from that of Debye,[2] who considers electrons at fixed distances from each other, of which equation (16) is the simplest example.

3. Comparison with Results of Quantum Mechanics.

Wentzel's equation (3a) for the intensity of the modified scattered rays[14] may be written in the form

$$I_{unm} = I_e\left\{\int \sum_n 4\pi r_n{}^2\rho_n\frac{\sin kr}{kr}dr\right\}, \tag{20}$$

where $\sum\rho_n = \sum u_n{}^2$ the electrical charge distribution in electronic units, the subscript indicating the n^{th} quantum number. Noting that $\sum 4\pi r^2\rho_n$ is numerically equal to our $Zu(r)$, this may be written

$$I_{unm} = I_e \cdot Z^2\left\{\int u(r)\frac{\sin kr}{kr}dr\right\}^2. \tag{21}$$

[14] G. Wentzel, reference 7, p. 781.

His equation (4a) for the intensity of the modified scattered rays (uncorrected for the change of wave-length) may similarly be written

$$I_{\text{mod}} = I_e\left\{Z - \sum\left[\int 4\pi r^2\rho_n \frac{\sin kr}{kr} dr\right]^2\right\}. \tag{22}$$

The total intensity of the scattered rays thus becomes,

$$\begin{aligned} I_s &= I_{\text{unm}} + I_{\text{mod}} \\ &= I_e\left\{Z - \sum\left[\int 4\pi r^2\rho_n \frac{\sin kr}{kr} dr\right]^2 + Z^2\left[\int u(r) \frac{\sin kr}{kr} dr\right]^2\right\}. \end{aligned} \tag{23}$$

This expression becomes identical with equation (18) if

$$4\pi r^2\rho_n = u(r). \tag{24}$$

We have noted above that

$$\sum_1^Z 4\pi r^2\rho_n = Zu(r), \tag{25}$$

whence relation (24) holds if

$$\sum_1^Z 4\pi r^2\rho_n = Z \cdot 4\pi r^2\rho_n, \tag{26}$$

i.e. if the charge distribution for every electron is the same. This is precisely the assumption on which equation (18) is derived. Wentzel, in his numerical calculation of equation (22) takes

$$\rho_n = u_n^2 \tag{27}$$

as the charge density for the nth electron, instead of

$$\rho_n = (1/Z) \sum_1^Z u_n^2, \tag{28}$$

which is the equivalent of (26). This introduces a slight difference between the results of his calculation and that of ours. It would seem however that relation (28) is in better accord with present interpretation of quantum mechanics than is (27), and if its validity is admitted, our classical equation (18) becomes identical with Wentzel's quantum equation (23).

This comparison shows that if we interpret $\sum u_n^2 dxdyd\underset{\sim}{z}$ as the electric charge in the volume element, the scattering which we calculate is the *unmodified* scattering (eq. 21). If, however, we intrepret it as the probability that a discrete electron will be present in the volume element, as we have done in deriving equation (18), we calculate the *total* scattering. Since the total scattering is experimentally observed, it would seem that the latter interpretation has the better physical justification.

In his derivation of equation (22), Wentzel has assumed the limiting case of very long wave-lengths, for which the scattering by a free electron is identical with that calculated on the classical theory. For shorter wave-lengths

Breit[15] and Dirac[16] have shown that the intensity of the modified rays from free electrons is reduced in the ratio

$$\frac{I_{\text{mod}}}{I_{\text{class}}} = \left(\frac{\lambda}{\lambda'}\right)^3 = (1 + \gamma \text{ vers } \phi)^3, \tag{29}$$

where λ and λ' are the wave-lengths of the primary and the modified ray respectively, and $\gamma = h/mc\lambda$. We may accordingly expect to get a closer approximation to the intensity of the modified scattering if we multiply equation (22) by equation (29), or using the equivalent part of equation (18),

$$I_{\text{mod}} = ZI_e(1 - F^2/Z^2)(1 + \gamma \text{ vers } \phi)^{-3}. \tag{30}$$

Similarly[17]

$$I_{\text{unm}} = I_e F^2, \tag{31}$$

where

$$F \equiv Z\int_0^a u(r)\frac{\sin kr}{kr}dr, \tag{32}$$

which is identical with the so-called "atomic structure factor."

A convenient method of comparing the experiments with the theoretical calculations is thus to multiply the observed intensity of the modified rays by the factor $(1+\gamma \text{ vers } \phi)^3$, and add to the observed intensity of the unmodified rays. The resulting value

$$I_s' = I_{\text{mod}}(1 + \gamma \cos \phi)^3 + I_{\text{unm}} \tag{33}$$

may then be compared directly with the value of I_s derived by the classical equation (18).

4. Analysis of Scattering Data to Determine Radial Electron Distribution

If the distribution of the electrons is spherically symmetrical, as we have assumed, we may represent the probability that an electron will lie between r and $r+dr$ by a Fourier sine series of the form,

$$u(r) = A_1 r \sin \pi r/a + A_2 r \sin 2\pi r/a + \cdots + A_n r \sin n\pi r/a + \cdots \tag{34}$$

Substituting this value of $u(r)$ in equation (19) we get,

$$S = 1 + (Z - 1)\left[\sum_1^\infty{}_n \int_0^a \frac{A_n}{k} \sin\left(n\pi\frac{r}{a}\right) \sin (kr)dr\right]^2. \tag{35}$$

If the scattering I_s is evaluated for $k = n\pi/a$, i.e., by equation (17) for

$$\sin (\phi/2)/\lambda = n/4a, \tag{36}$$

[15] G. Breit, Phys. Rev. **27**, 242 (1926).

[16] P. A. M. Dirac, Proc. Roy. Soc. **111**, 405 (1926). This relation (29) presumably does not hold for wave-lengths so short that the velocity of the recoil electron approaches c. In this case the formula of Klein and Nishina presents a closer approximation.

[17] It is interesting that the ratio $I_{\text{mod}}/I_{\text{unm}}$ is expressed by equations (30 and (31) in terms of interference. It was early suggested by the writer (Phil. Mag. **46**, 910 (1923)) that this ratio might be thus expressed, as an alternative to the more obvious description developed later by Jauncey, in terms of the ratio of the energy of recoil of the scattering electron to its binding energy in the atom. Wentzel[7] shows that equivalent expressions of the ratio I_u/I_m may be made in terms of either interference or energy of recoil.

where a is an assumed maximum radius, all integrals in the sum of equation (35) vanish except the nth, giving

$$S_n = 1 + (Z-1)\left[\frac{1}{4}\frac{a^2}{k^2}A_n^2\right]. \tag{37}$$

Thus

$$A_n = \pm\frac{2k}{a}\left\{\frac{S_n-1}{Z-1}\right\}^{1/2}. \tag{38}$$

Corresponding to each value of S_n we thus determine the nth term of the Fourier series (34), and thus eventually the value of $u(r)$.

Our series (34) has in it an arbitrary radius a, and in evaluating the series the data for only certain arbitrarily chosen values of k are employed. If this arbitrary radius is made large, the values of k which are used come closer together, and our series approaches the Fourier integral,

$$u(r) = r\int_0^\infty B\sin(\pi rx)dx, \tag{39}$$

where

$$x \equiv n/a = (4/\lambda)\sin(\phi/2), \tag{40}$$

according to equation (36), and

$$B \equiv A_x a = 2\pi x\left\{\frac{S_x-1}{Z-1}\right\}^{1/2}. \tag{41}$$

If instead of the probable position of a single electron, we wish to find the probable number of electrons between r and $r+dr$, we have only to multiply $u(r)$ by the number of electrons per atom, giving by equation (34)

$$U(r) = Zu(r) = Zr\sum_1^\infty A_n\sin n\pi r/a, \tag{42}$$

or by (39),

$$U(r) = Zr\int_0^\infty B\sin(\pi rx)dx. \tag{43}$$

It is interesting to compare equation (42) with the similar series expressing the radial distribution of electrons in the atoms of a crystal,[1]

$$U(r) = 8\pi\frac{r}{D^2}\sum_1^\infty nF_n\sin 2\pi n\frac{r}{D}. \tag{44}$$

We note that a of equation (42) corresponds to $D/2$ of (44), since both quantities represent the assumed outer limit of the atom. The series are accordingly identical if $2\pi(r/a^2)nF_n = ZrA_n$. Using the value of A_n given by (38), and noting that $D = 2a = (n\lambda/2)\sin\frac{1}{2}\phi$, this means that

$$F_n = Z\left\{\frac{S_x-1}{Z-1}\right\}^{1/2}. \tag{45}$$

This expression enables us to compare the "F" curves obtained from crystal reflection with the data given by scattering experiments.

[18] A. H. Compton, "X-rays and Electrons," p. 164. An integral identical in form with (43), but representing the electron distribution in atoms of a crystal, has been given by G. E. M. Jauncey and W. D. Claus, Phys. Rev. **32**, 20 (1928).

5. Tests of the Method of Analysis

Before applying equation (43) to the interpretation of experimental data, it will be of interest to study its application to certain cases where the solution is known.

a. Consider the intensity distribution described by equation (15). From equations (15) and (41) we have

$$B = \pm (2/a) \sin \pi x a. \tag{46}$$

Substituting this value in (43), since $Z = 2$,

$$U = 4(r/a) \int_0^\infty \sin (\pi a x) \sin (\pi r x) dx. \tag{47}$$

This integral is zero,[19] except when $r = a$, in which case its value becomes infinite, indicating a concentration of the electrons at the distance $r = a$ from the nucleus, in accord with the original assumption on which (15) was based.

b. An atom of four electrons, each of whose probability of lying between r and $r+dr$ is $u(r) = 2r/a^2$ between $r = 0$ and $r = a$, and is zero beyond $r = a$.

By equation (19) we find,

$$S = 1 + 3\left\{\frac{2(1 - \cos \pi x a)}{\pi^2 x^2 a^2}\right\}^2. \tag{48}$$

From (41) then,

$$B = \pm \frac{4}{\pi x a^2}(1 - \cos \pi x a),$$

and equation (39) becomes,

$$u(r) = 4\frac{r}{a}\left\{\int_0^\infty \frac{\sin \pi r x}{\pi a x} dx - \int_0^\infty \frac{\cos \pi a x \sin \pi r x}{\pi a x} dx\right\}. \tag{49}$$

The value of the integrals is[20] $1/2a$ for $[r < a]$, and 0 for $[r > a]$, whence

$$\begin{aligned} u(r) &= 2r/a^2 \qquad [r < a], \\ &= 0 \qquad\quad [r > a], \end{aligned} \tag{50}$$

as initially assumed.

These tests check the accuracy of the mathematical analysis. They of course say nothing, however, regarding the validity of our physical assumptions of spherical symmetry and of independence of the positions of the various electrons in the atomic groups.

6. Electron Distribution in Helium

The formulas that have been developed above are directly applicable only to the scattering of x-rays by gases, in which case the interference effect due to neighboring molecules is negligible. In the case of the noble gases we are also free from interference between adjacent atoms, since the gases are mona-

[19] At any point when $r \neq a$ the integral is strictly speaking indeterminate; but its average value over a finite range of x is zero.

[20] B. O. Peirce, "A Short Table of Integrals" (1910) nos. 484 and 485.

tomic, and according to current theories the probable electron distributions should be spherically symmetrical as we have assumed in our calculations. Fortunately recent experiments by Barrett[21] supply sufficient information regarding the scattering by helium to yield valuable information.

In Barrett's Fig. 7 he compares the scattering by helium with that by hydrogen, which he finds identical with that calculated from the Breit-Dirac quantum formula for the range investigated. With an effective wave-length of 0.49A, he finds that helium and hydrogen scatter equally, within experimental error, at angles greater than 60°, but that at 40°, 30° and 20° the scattering by helium is greater by the ratios 1.025, 1.08 and 1.26 respectively. These values are indicated by the circles in Fig. 3, where $S \equiv I_s/ZI_e$ is plotted against x. At sufficiently small angles the phase difference between the rays from the two electrons in helium must be negligible, in which case our theory demands that the value of S must approach *2*. For small values of x the phase

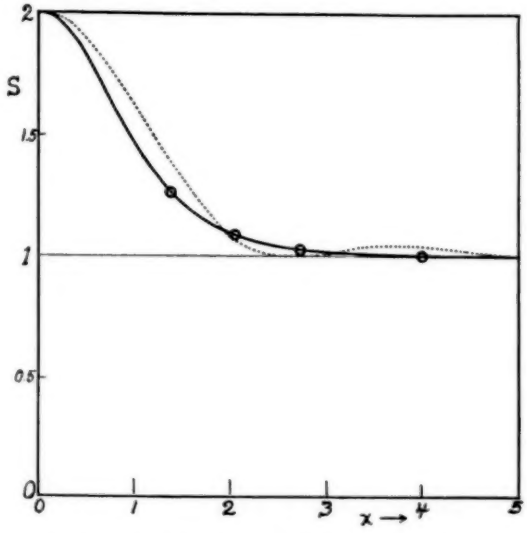

Fig. 3. Solid line, relative scattering by helium, based on Barrett's data (circles). Broken line, calculated scattering by Bohr type helium atom.

differences are small quantities of the first order; but the amplitudes, being proportional to the cosines of the phase differences, are affected only in the second order of small quantities.[22] Thus the S curve must leave the $x=0$ axis parallel to the x axis, and must initially be of a parabolic form.[23] We can thus interpolate the S curve between $x=0$ and $x=1.4$ with some degree of assurance as indicated by the solid line.

This S curve can be transformed into a B curve by the help of equation (41), giving the result shown in Fig. 4. Here again the values given by the experimental data are shown by the circles.

[21] C. S. Barrett, Phys. Rev. **32,** 22 (1928).

[22] This may be seen by finding the maximum value of E from equation (5) for small values x_n. This maximum is unaffected to the first power of x_n, but is reduced by terms containing x_n^2.

[23] These conclusions are valid only if the atom is not of infinite extent.

For values of x greater than 3 the experiments suggest that B gradually approaches zero.[24] The values of the integral U are not much affected by the exact manner of this approach as long as it is slow and continuous. For con-

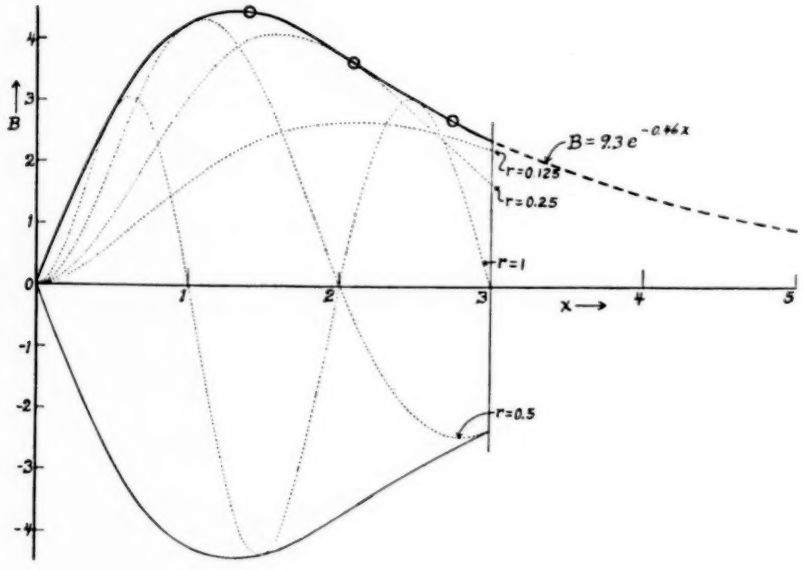

Fig. 4.

venience, therefore, we may assume that beyond some arbitrary value of x, say x_1, B may be expressed by

$$B = be^{-ax} \quad [x > x_1]. \tag{51}$$

In order that at $x = x_1$ the values of B and dB/dx shall be continuous, we must have

$$a = -\left(\frac{1}{B}\frac{dB}{dx}\right)_{x_1} \tag{52}$$

and

$$b = B_1 e^{ax_1} \tag{53}$$

In order to evaluate $U(r)$ for a definite value of r we must determine the integral,

$$\Phi = \int_0^\infty B \sin(\pi r x) dx. \tag{54}$$

This may be separated into two parts,

$$\Phi_1 \equiv \int_0^{x_1} B \sin(\pi r x) dx, \tag{55}$$

and

$$\Phi_2 \equiv \int_{x_1}^\infty B \sin(\pi r x) dx. \tag{56}$$

[24] B must approach zero for large values of x unless the electron density at the center of the atom is infinite.

The first part Φ_1 may be evaluated graphically, by plotting $B \sin(\pi r x)$ for various values of r, as indicated by the dotted lines of Fig. 4, and integrating from O to x_1 with a planimeter. Φ_2 may be determined by substituting in equation (56) the value of B given in equation (51) and integrating, which gives

$$\Phi_2 = B_1 \frac{a \sin \pi r x_1 + \pi r \cos \pi r x_1}{a^2 + \pi^2 r^2}. \tag{57}$$

From Fig. 4 we find for helium, if $x_1 = 3$, $B_1 = 2.36$ and $a = 0.46$, whence the value of Φ_2 may be determined for any desired value of r.

As typical examples, we have the following values (Table I):

TABLE I.

r	Φ_1	Φ_2	$\Phi = \Phi_1 + \Phi_2$	$U = Zr\Phi$
1.125A	5.75	1.64	7.39	1.85
0.25	8.16	−0.42	7.74	3.87
0.5	3.14	−0.35	2.79	2.79
1.0	0.86	−0.70	0.16	0.32

The resulting values of U plotted against r are shown in Fig. 5 by the solid line.

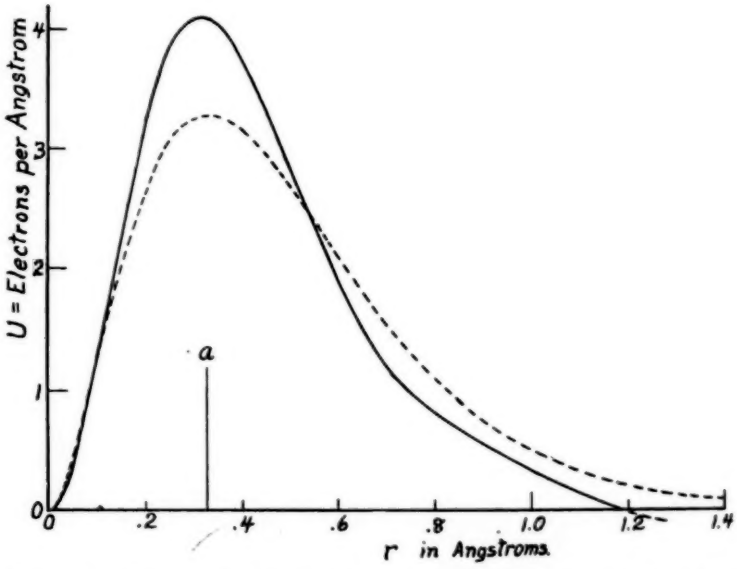

Fig. 5. Radial electron distribution in helium. Solid line, based on Barrett's x-ray scattering data. Broken line, Pauling's calculation from wave mechanics. a = radius of Bohr orbits.

It is of great interest to compare the "observed" distribution with that calculated theoretically. According to the Bohr-Sommerfeld theory, the elec-

trons in helium should both traverse approximately circular orbits with unit angular momentum, the radius of the orbits being given by

$$a = h^2/[4\pi^2 e^2 m(Z - s)]. \tag{58}$$

where h, e, m and Z have their usual significance, and s is the "screening constant" of each electron on the other, having a value[25] of approximately $s = 0.39$. Using the usual values of the constants, we thus find $a = 0.33$A. It will be seen that this value falls very close to the radius of maximum electron density as shown in Fig. 5.

If we assume that the two electrons are on a spherical surface of fixed radius $r = 0.33$A, the intensity of the scattered rays should be given by equation (15). The values of s thus calculated are shown by the dotted line Fig. 3. The differences between this dotted curve and the experimental points are considerably greater than the probable experimental error. Yet it is not impossible that a combination of heterogeneous x-rays such as Barrett used and the presence of incoherent rays (Compton scattering) at the large angles might flatten out the dotted curve to resemble the experimental one.

The distribution found from this analysis of Barrett's scattering data is however in striking agreement with that calculated on Schrödinger's wave mechanics. Thus Pauling[25] has shown that the radial electron distribution in helium can be expressed to a close approximation by

$$U(r) = Zr^2X^2, \tag{59}$$

where for helium in the normal state he finds,

$$X = u_{1,0} = -2\left(\frac{Z - s}{a_0}\right)^{3/2} e^{-\xi/2} \tag{60}$$

$$a_0 = h^2/4\pi^2 e^2 m = 0.53A,$$

$$Z = 2$$

$$s = \text{screening const} = 0.39$$

$$\xi = 2(Z - s)r/a_0.$$

Substituting these values in equation (59) we get the U curve shown by the dotted line of Fig. 5. The striking similarity between this distribution predicted by the quantum theory and that coming from our interpretation of the scattering experiments is the more convincing when it is noted that there are no arbitrary constants available to make the two curves correspond. This agreement is a strong argument in favor of a continuous electron distribution, as predicted by the wave-mechanics, as opposed to the Bohr quantum theory of definite orbits.

[25] Cf. e.g. L. Pauling, Proc. Roy. Soc. **A114,** 181 (1927).

TWO NOTES ON THE PROBABILITY OF RADIATIVE TRANSITIONS

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Abstract

In 1 we compute the rate at which electrons and protons should, on Dirac's theory of electrons and protons, annihilate each other; this gives a mean life time for matter of the order of 10^{-10} sec.

In 2 we compute by Dirac's radiation theory the relative probability of radiative and radiationless transitions; we obtain an expression substantially equivalent to that derived by Heisenberg and Pauli.

I

AN ELECTRON satisfying Dirac's linear wave equation will very rapidly lose energy to the electromagnetic field. If the electron is free, it must lose this energy by radiating at least two quanta, in order that energy and momentum may be conserved in the process. If the electron is bound, e.g. in an atom, transitions in which only one quantum is radiated can occur, since there are then other particles present which can take up the necessary momentum. But these transitions are rare compared with the two-quantum transitions, which, as is well known, may be expected according to the theory to occur at an infinite rate. Now Dirac has suggested[1] that the reason why these transitions do not in fact occur is that the states of negative energy are filled; and this suggestion leads to a satisfactory understanding of the validity of the scattering laws derived from his wave equation. But according to Dirac not all of the states of negative energy are full; there are a few gaps in the distribution for negative electrons nearly at rest; and thus transitions to states of negative energy should not be quite excluded. Dirac further suggests that the empty states of negative energy are protons; and thus the filling of these states should correspond to the annihilation of an electron and a proton. This should occur very rarely; and if Dirac's suggestion were correct, we should expect to find a very small value for the corresponding transition probability. In this note we shall compute this transition probability on the basis of the present theory.

This computation cannot be made theoretically unique and certain until the grave difficulties introduced by the inequality of electron and proton masses are resolved; and this resolution seems to demand an essential advance[2] in the theory. The chief ambiguity for the present work arises from the fact that the energy radiated by the conversion of a stationary positive elec-

[1] P. A. M. Dirac, Roy. Soc. Proc. **A126,** 360 (1930).
[2] J. R. Oppenheimer, Phys. Rev. **35,** 461 (1930).

tron into a stationary negative electron is $2mc^2$; whereas the energy liberated by the annihilation of a stationary electron and a stationary proton should be $(m+M_P)c^2$. We shall make the computation without explicit recognition of the difference in mass of electron and proton; this gives a transition probability which is absurdly large, and which is not appreciably reduced by the substitution of $m+M_P$ for $2m$ in the final formula.

Let us consider for definiteness an enclosure of volume V in which there is one free electron, and one gap in the negative energy distribution; and let both the electron and the gap be at rest. If electron and proton have in fact a relative velocity v, then our result will be in error by terms of the relative order $(v/c)^2$. For the wave equation of the electron we write

$$\{W/c + \alpha_0 mc + (h/2\pi i)[\alpha_1(\partial/\partial x) + \alpha_2(\partial/\partial y) + \alpha_3(\partial/\partial z)]\}\psi = 0 \tag{1}$$

We take the matrices $||\alpha_\mu(\rho\sigma)||$ in the form

$$\begin{aligned}
\|\alpha_1(\rho\sigma)\| &= \begin{Vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{Vmatrix}; \quad \|\alpha_2(\rho\sigma)\| = \begin{Vmatrix} 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{Vmatrix} \\
\|\alpha_3(\rho\sigma)\| &= \begin{Vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{Vmatrix}; \quad \|\alpha_0(\rho\sigma)\| = \begin{Vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{Vmatrix}
\end{aligned} \tag{2}$$

The normalized solutions corresponding to momenta p, q, r, and energy W given by

$$(W/c)^2 = m^2c^2 + p^2 + q^2 + r^2 \tag{3}$$

may then be written

$$\begin{aligned}
\psi_3{}^\alpha &= 0; \\
\psi_4{}^\alpha &= \frac{(mc + W/c)e^{2\pi i/h(px+qy+rz)}}{[(mc + W/c)^2 + p^2 + q^2 + r^2]^{1/2}V^{1/2}} \\
\psi_1{}^\alpha &= \frac{-(p + iq)e^{2\pi i/h(px+qy+rz)}}{[(mc + W/c)^2 + p^2 + q^2 + r^2]^{1/2}V^{1/2}}; \\
\psi_2{}^\alpha &= \frac{re^{2\pi i/h(px+qy+rz)}}{[(mc + W/c)^2 + p^2 + q^2 + r^2]^{1/2}V^{1/2}}
\end{aligned}$$

and

$$\begin{aligned}
\psi_4{}^\beta &= 0; \qquad \psi_3{}^\beta = \psi_4{}^\alpha \\
\psi_1{}^\beta &= -\psi_2{}^\alpha; \quad \psi_2{}^\beta = \bar{\psi}_1{}^\alpha.
\end{aligned} \tag{4}$$

The two wave functions for α and β give electrons with spin oriented parallel and antiparallel respectively to the z axis.

For the initial state of the electron we take

$$W = E_0 = h\nu_0 = mc^2;\ \psi_1^0 = \psi_2^0 = 0;\ \psi_3^0 = e^{2\pi i\gamma}(2V)^{-1/2};\ \psi_4^0 = (2V)^{-1/2} \quad (5)$$

similarly for the final state we take

$$\begin{aligned} W &= E^e = -h\nu_0 = -mc^2; \quad & \psi_3^e &= \psi_4^e = 0; \\ \psi_1^e &= e^{2\pi i\delta}(2V)^{-1/2}; & \psi_2^e &= (2V)^{-1/2}. \end{aligned} \quad (6)$$

Here γ and δ are independent indeterminate phases; if in the final results we average over these, we shall have assumed random orientations for the spins of both initial and final states; and with this understanding both (5) and (6) may be regarded as spherically symmetric.

We shall need also the wave functions for states with

$$p = q = 0;\ r = \pm mc;\ W = \pm (2)^{1/2}mc^2.$$

These are

$$\psi_2^\alpha = \psi_4^\alpha = 0;\ \psi_1^\alpha = \frac{-re^{\pm 2\pi imcz/h}}{mcV^{1/2}(4 \pm 2(2)^{1/2})^{1/2}};\ \psi_3^\alpha = \frac{(1 \pm (2)^{1/2})e^{\pm 2\pi imcz/h}}{V^{1/2}(4 \pm 2(2)^{1/2})^{1/2}}$$

and

$$\psi_1^\beta = \psi_3^\beta = 0;\ \psi_2^\beta = -\psi_1^\alpha;\ \psi_4^\beta = \psi_3^\alpha. \quad (7)$$

Initially there is to be no radiation present; the electron is in the state (0). The probability amplitude at a later time t that a quantum of frequency ν, momentum $\boldsymbol{p}$, and electric vector polarized along the unit vector $\boldsymbol{\epsilon}$, shall have been emitted, and that the electron shall have jumped to a state of momentum $\boldsymbol{P}$, energy $h\bar{\nu}$, and polarization of spin $\tau = \alpha, \beta$, is then

$$\phi(\boldsymbol{p},\boldsymbol{\epsilon};\ \boldsymbol{P},\bar{\nu},\tau) = -v(0;\boldsymbol{p},\boldsymbol{\epsilon},\bar{\nu},\tau)\frac{1 - e^{2\pi i(\nu+\bar{\nu}-\nu_0)t}}{\nu + \bar{\nu} - \nu_0}. \quad (8)$$

Here $v(o;\ \boldsymbol{p},\ \boldsymbol{\epsilon},\ \bar{\nu},\ \tau)$ is the matrix component for the transition in question of the interaction energy between the electron and the light quantum field. This vanishes except when $\boldsymbol{P} = -\boldsymbol{p}$, and for $\boldsymbol{P} = -\boldsymbol{p}$ has the value

$$ec(2\pi/\nu hV)^{1/2}\left(\sum_{l=1}^{3}\epsilon_l\alpha_l e^{-2\pi i/h(\mathbf{P}\cdot\mathbf{r})}\right)0;\ \bar{\nu},P,\tau;\ \text{with}\ \bar{\nu}^2 = \nu_0^2 + \nu^2 \quad (9)$$

where

$$\left(\sum_{l=1}^{3}\epsilon_l\alpha_l e^{-2\pi i/h(\mathbf{P}\cdot\mathbf{r})}\right)0;\ \bar{\nu},P,\tau$$

is the matrix component corresponding to the electronic transition

$$(0) \rightarrow (\bar{\nu},P,\tau)$$

of the component of the vector

$$\boldsymbol{\alpha}e^{-2\pi i/h(\mathbf{P}\cdot\mathbf{r})}$$

parallel to $\boldsymbol{\epsilon}$.

The probability amplitude that the electron should have jumped to state (e), and that a second quantum of frequency ν', momentum $\boldsymbol{p}'$, and polarization along $\boldsymbol{\varepsilon}'$ should have been emitted, vanishes except when $\boldsymbol{p}' = -\boldsymbol{p} = \boldsymbol{P}$, and for $\boldsymbol{p}' = \boldsymbol{P}$ has the value

$$\phi(\boldsymbol{p},\boldsymbol{\varepsilon},\boldsymbol{p}',\boldsymbol{\varepsilon}';\, e) = \frac{2\pi e^2 c^2}{h\nu V} \sum \left\{ \frac{1-e^{2\pi i(\nu-\bar{\nu}-\nu_0)t}}{\nu-\bar{\nu}-\nu_0} - \frac{1-e^{4\pi i(\nu-\nu_0)t}}{2(\nu-\nu_0)} \right\}$$

with

$$\sum = \sum_{\bar{\nu}} \sum_{l} \left\{ \left(\sum_{e=1}^{3} \epsilon_l \alpha_l e^{-2\pi i/h(\boldsymbol{p}.\boldsymbol{r})} \right)_{0;\bar{\nu},P\tau} \left(\sum_{l=1}^{3} \epsilon_l' \alpha_l e^{2\pi i/h(\boldsymbol{p}.\boldsymbol{r})} \right)_{\nu,P,\tau;e} \right.$$

$$\left. + \left(\sum_{l=1}^{3} \epsilon_l' \alpha_l e^{2\pi i/h(\boldsymbol{p}.\boldsymbol{r})} \right)_{0;0,P,\tau} \left(\sum_{l=1}^{3} \epsilon_l \alpha_l e^{-2\pi i/h(\boldsymbol{p}.\boldsymbol{r})} \right)_{0,P\tau;e} \right\} (\nu+\bar{\nu}-\nu^{-1}) \tag{10}$$

This grows large only for $\nu \sim \nu_0$, $\bar{\nu} \sim \pm (2)^{1/2}\nu_0$; and here the first term in the bracket may be neglected.

To evaluate $\sum$ for $\nu = \nu_0$, $\bar{\nu} = \pm (2)^{1/2}\nu_0$, we may without loss of generality take $\boldsymbol{p}$ along z, since both initial and final wave functions are effectively spherically symmetric. We may further take, again without loss of generality, $\boldsymbol{\varepsilon}$ along x. There are then two cases to consider, with $\boldsymbol{\varepsilon}'$ along x and along y respectively. For these cases we have in turn

$$\sum = \sum_{\bar{\nu}=\pm(2)^{1/2}\nu_0} \sum_{\tau=\alpha,\beta} \bar{\nu}^{-1} \left\{ \left[\int dV \sum_{p,\sigma} \bar{\psi}_\sigma^{\bar{\nu},P,\tau} e^{-2\pi i/c.\nu_0 z} \alpha(\sigma\rho) \psi_\rho^{\,0} \right\} \right.$$

$$\left\{ \int dV \sum_{\rho\sigma} \psi_\sigma^{\,e} e^{2\pi i/c\nu_0 z} \begin{Bmatrix} \alpha_1(\sigma,\rho) \\ \alpha_2(\sigma,\rho) \end{Bmatrix} \psi_\rho^{\bar{\nu},P,t} \right\} \tag{11}$$

$$\left. + \left\{ \int dV \sum_{\rho\sigma} \bar{\psi}_\sigma^{\nu,P\tau} e^{2\pi i/c.\nu_0 z} \begin{Bmatrix} \alpha_1(\sigma,\rho) \\ \alpha_2(\sigma\,,\,\rho) \end{Bmatrix} \psi_\rho^{\,0} \right\} \left\{ \int dV \sum_{\rho\sigma} \bar{\psi}_\sigma^{\,e} e^{-2\pi i/c.\nu_0 z} \alpha_1(\sigma,\rho) \psi_\rho^{\bar{\nu},P,\tau} \right\} \right].$$

If we use (2) and (7) this gives us

$$\begin{aligned} \sum &= 0 \text{ for } \boldsymbol{\varepsilon}' \| x \\ \sum &= (-i/2\nu_0)(1 + e^{2\pi i(\gamma-\delta)}) \text{ for } \boldsymbol{\varepsilon}' \| y. \end{aligned} \tag{12}$$

From this we conclude that the probability of an emission is proportional to the square of the sine of the angle between the electric vectors of the two quanta.

Now there are $2\nu_0^2(V/c^3)$ components of the radiation field per unit solid angle per unit frequency about ν_0; the direction of propagation of one quantum can vary over a hemisphere; but when this is fixed polarization, frequency and direction of propagation of the other quantum are determinate. Thus we get the total chance of an emission at time t by integrating the absolute value of the square of ϕ (averaged over γ and δ) over a hemisphere of solid angle and all frequencies, and multiplying by $2\nu_0^2(V/c^2)$; thus

$$\sum_{p,\epsilon} \int d\gamma \int d\delta \, |\, \phi(\boldsymbol{p},\boldsymbol{\epsilon}, -\boldsymbol{p},\boldsymbol{\epsilon}'; e) \,|^2$$

$$= \frac{4\pi\nu_0^2 V}{c^3} \cdot \frac{e^4c^4 \cdot 4\pi^2}{h^2\nu_0^2V^2} \cdot \frac{1}{2\nu_0^2} \cdot \int_0^\infty \frac{d\nu \,|\, 1 - e^{4\pi i(\nu-\nu_0)t} \,|^2}{4(\nu-\nu_0)^2}$$

$$= t \cdot \frac{16\pi^4e^4c}{h^2\nu_0^2V} \cdot \int_{-\infty}^{\infty} \frac{1-\cos x}{x^2} dx \tag{13}$$

$$= t \cdot \frac{16\pi^5e^4}{m^2c^3V} \cdot$$

The mean life time of an electron in a proton density of n_P protons per unit volume is thus

$$T = \frac{m^2c^3}{16\pi^5e^4n_P} \sim \frac{5\times10^{10}}{n_p} \text{ sec.} \tag{14}$$

It should be observed that the retention of the terms for $\bar{\nu} = -2^{1/2}\nu_0$ in the expression (11) for $\sum$, may be justified by an argument similar to that used by Dirac to validate the scattering formulae. For although the electron cannot jump to this state of negative energy, because it is already filled, there is a double transition which gives just the same terms in $\sum$, and in which first a negative electron in the state $(-2^{1/2}\nu_0, P, \tau)$ jumps to a state near the state (0), and then the original positive electron jumps down from the state (0) to the state $(-2^{1/2}\nu_0, P, \tau)$; in either transition either of the two quanta may be emitted.

If we try to correct (13) to take account of the fact that the energy radiated should be $(m+M_P)c^2$ and not $2mc^2$, we get in place of (14)

$$T' = \frac{(m+M_p)^2c^3}{64\pi^5e^4n_p} \sim \frac{5\times10^{16}}{n_p} \text{ sec.} \tag{15}$$

Both (14) and (15) give an absurdly short mean life time for matter. With $n_P = 10^{25}$ we get

$$T \sim 5 \times 10^{-15}; \quad T' \sim 5 \times 10^{-9}.$$

Of course the protons and electrons of matter are not in general free, nor uniformly distributed, nor at rest. But we should hardly expect their agglomeration into nuclei, or even atoms, to reduce appreciably the mean transition probability, since this would mean essentially an increase in the effective n_P to be used. In any case (14) or (15) should apply roughly to electrons and protons in a discharge tube.

II

In their paper on the relativistic treatment of the interaction of radiation and matter, Heisenberg and Pauli point out that according to their theory the radiationless transitions of the quantum mechanics may always be expected

to be accompanied by transitions which correspond to a change in the material system and the emission of at least one quantum of light.[3] So, for example, in the Auger jumps, in the ionization of an atom in an electric field, in the capture of electrons by alpha-particles, and in the radioactive decay of nuclei, the energy of the liberated particles should show a certain diffuseness; and energy is only conserved by the emission of an appropriate continuous distribution of light. Heisenberg and Pauli derive an expression for the probability of such transitions involving radiation; they show that this probability is small, compared with that of the radiationless transitions, of the order

$$e^2/hc \ (v/c)^2.$$

They apply this result to the problem of radioactive disintegration, where the escape of the alpha and beta particles may be roughly schematized as a diffusion through a high wall of potential energy; and they obtain so an explanation of the sharp definition of the energies of alpha-particles, and the great diffuseness of the beta spectrum. The non-appearance of the gamma radiation, which, on this theory, should accompany beta-ray disintegration, remains unexplained.

In this note we shall compute the relative probability of such radiative transitions on the basis of the Dirac radiation theory. For this probability we obtain an expression which, in the approximation to which the calculations of H. P. were carried, should agree with the results of that calculation. In our formula certain terms appear which were deliberately neglected in H. P.; and further this formula is applicable to a slightly more general group of problems than that of H. P., which cannot strictly be applied to any of the problems mentioned above except that of the Auger jumps; but except for these minor modifications our result reduces to that of H. P.; and it gives the same predictions when applied to the theory of radioactive disintegration. The present work is rather simpler than that on the basis of the more general theory.

For the occurrence of radiationless transitions it is essential that the material system (and we shall call this the "atom") be in a quasistationary state of an energy equal to the energy of some aperiodic motion of the system. Let the wave equation for the atom,—which may be written in the configuration space, and without explicit reference to the radiation field, to the order $(v/c)^2$—be

$$(H - h\nu)\psi_\nu = 0. \tag{16}$$

Let the initial state have the energy

$$E_0 = h\nu_0 \tag{17}$$

and be given by a wave packet which satisfies the equation

$$(H - V - h\nu_0)\psi_0 = 0. \tag{18}$$

[3] W. Heisenberg and W. Pauli, Zeits. f. Physik **56**, 1 (1929); cited as H. P.

The wave packets for the quasistationary aperiodic states of the atom we call θ_ν; they satisfy

$$(H - V' - h\nu)\theta_\nu = 0;\ E = h\nu \tag{19}$$

and shall be normalized to $d\nu$. Then the probability of a radiationless transition to the continuum is given, to the first order in the small quantity λ_0/ν_0, by

$$\lambda_0 = 4\pi^2/h^2 \mid V_{\nu 0} \mid^2;\ V_{\nu 0} = \int d\tau \delta_{\nu_0} V \psi_0. \tag{20}$$

(The integral over $d\tau$ is to be taken over the configuration space of the atom.)

Now let there be no radiation present initially. Since the atom has energy levels lower than E_0, it can make radiative transitions to these states; Dirac's radiation theory gives us, for the probability per unit time per unit frequency ν_s of the radiation, for this transition

$$\lambda_s d\nu_s = 16\pi^2 \nu_s d\nu_s / 3hc^3 \mid \dot{P}_{\nu_0 - \nu_s, 0} \mid^2$$

with

$$\dot{P}_{\nu_0 - \nu_s, 0} = \int d\tau \bar{\theta}_{\nu_0 - \nu_s} \dot{P} \psi_0 \tag{21}$$

where $\dot{P}$ is the time rate of change of the electric moment of the atom. (With Dirac's linear Hamiltonian for the electron it will be

$$\sum_R e_k \boldsymbol{\alpha}^k$$

where e_k is the charge on the k'th particle, and the α^ks are the Dirac matrices, and the summation is to be taken over all particles.)

Now when V is not very small, (21) gives us only a very poor approximation for the probability of the corresponding transitions. Somewhat inaccurately we may say that the system can reach the same final state by a double jump, in which, e.g., the atom goes over into some arbitrary state in the continuum, and then—but there is no interval between the jumps,—jumps to the final state and emits a quantum. In this process of course only the total energy of the system is conserved, and that only when one considers the double jump as a single process. This is the effect treated by H. P.; and to obtain it we have only to carry the perturbation theory a step farther than was necessary for the derivation of (20) and (21).

The Dirac wave equation for the probability amplitude ϕ for the whole system, taken as a function of the state, which for brevity we describe by the single index ν, of the atom, and the number N_{ps} of quanta of frequency ν_s, polarization p, and given direction of propagation, is

$$
\begin{aligned}
-h/2\pi i\cdot\partial/\partial t\phi(\nu,N_{sp}) &= \sum_{\nu' N' s p} H(\nu,N_{sp};\nu' N'_{sp})\phi(\nu',N'_{sp}) \\
&= \int d\nu' V''_{\nu\nu'}\phi(\nu',N_{sp}) + V_{\nu 0}\phi(0,N_{sp}) \\
&+ \int d\nu' \sum_{s'p'} N_{s'p'}^{1/2}\nu_{s'}^{1/2}\kappa_{s'p'}^{1/2}(\boldsymbol{e}_{s'p'}\cdot\dot{\boldsymbol{P}}_{\nu\nu'})\phi(\nu',N_{sp}-\delta_{ss'}\delta_{pp'}) \\
&+ \int d\nu' \sum_{s'p'}(N_{s'p'}+1)^{1/2}\nu_{s'}^{1/2}\kappa_{s'p'}^{1/2}(\boldsymbol{e}_{s'p'},\dot{\boldsymbol{P}}_{\nu i'})\phi(\nu',N_{sp}+\delta_{ss'}\delta_{pp'})
\end{aligned}
\tag{22}
$$

with $$\kappa_{sp}=h/2\pi c^3\sigma_{sp}.$$

Here σ_{sp} is the number of components of the radiation field of given polarization per unit frequency about ν_s per unit solid angle for the direction of propagation; and $\boldsymbol{e}_p$ is a unit vector parallel to the electric vector of the component sp. The summation $\sum_{sp}$, and the product $\prod_{sp}$ infra, are to be taken over all the components of the field.

If we take for our initial conditions for ϕ

$$
\begin{aligned}
\phi(\nu,N_{sp}) &= 0 \\
\phi(0,N_{sp}) &= \prod_{sp}\delta(N_{sp},0)e^{-2\pi i\nu_s t}
\end{aligned}
\tag{23}
$$

and put these values in (7), we find in first approximation

$$
\begin{aligned}
\phi_1(\nu,N_{sp}) &= \prod_{sp}\delta(N_{sp},0)V_{\nu_0}\frac{e^{-2\pi i\nu t}-e^{-2\pi i\nu_0 t}}{h(\nu-\nu_0)} \\
&+ \sum_{s'p'}\delta(N_{s'p'},1)\prod_{s''p''}{}'\delta(N_{s''p''},0)\nu_{s'}^{1/2}\chi_{s'p'}^{1/2}(\boldsymbol{e}_{s'p'}\cdot\dot{\boldsymbol{P}}_{\nu_0})\frac{e^{-2\pi i(\nu+\nu_{s'})t}-e^{-2\pi i\nu_0 t}}{h(\nu+\nu_{s'}-\nu_0)}
\end{aligned}
\tag{24}
$$

In Π' the factor for $s''=s'$, $p''=p'$ is to be omitted.

If one puts this expression (24) for ϕ_1 in (22), integrates the equation to obtain the second approximation $\phi_2(\nu, N_{sp})$, and takes the sum over all components of the field

$$\sum_p\int d\nu_s\int d\omega_s\,|\,\phi_2(\nu,1_{sp})\,|^2,$$

this gives the probability that the system has, at time t emitted a quantum of frequency near $\nu_s=\nu_0-\bar{\nu}$, and made a transition to a state in the continuum of energy near $h\bar{\nu}$. The coefficient of t in this expression gives the transition probability for transitions to a state in the range $\bar{\nu}$ to $\bar{\nu}+\Delta\bar{\nu}$:

$$
\lambda_s(\bar{\nu})\Delta\bar{\nu} = \frac{16\pi^2\nu_s\Delta\bar{\nu}}{3c^3h^3}\left|h\dot{\boldsymbol{P}}_{0\bar{\nu}}-\int\frac{d\nu' V_{0\nu'}\dot{\boldsymbol{P}}_{\nu'\bar{\nu}}}{\nu_0-\nu'}-\int\frac{d\nu'\dot{\boldsymbol{P}}_{0\nu'}V'_{\nu'\bar{\nu}}}{\bar{\nu}-\nu'}\right|^2. \tag{25}
$$

The first term in the bracket is the direct emission given by (21) and neglected by H. P.; the remaining terms differ from those of H. P. (132) only by having

V' in place of V. When ψ_0 and θ_r are characteristic functions of the same equation, these terms reduce to those given in H. P.

It should be observed that both (25) and H. P. (132) are derived as approximations; in particular, the momentum of the light quantum, and terms of higher order in v/c, are neglected in both computations. The retention of this momentum leads to the same modification in (25) and H. P. (132); and so does the retention or terms of the fourth order in v/c. But in higher orders only the method of H. P. can be used, since then no equation of the form (16) holds for the atom, and it is necessary to work directly from the more general equations of quantum electrodynamics, and take more complete account of the retardation of the forces between the particles of the atom.

To obtain the order of magnitude of the total radiative transition probability for radioactive disintegrations, we may observe that V and V' may be expected to be of the same order of magnitude as $h\nu_0$, and we integrate (25) for all frequencies ν_s up to ν_0; this gives

$$\lambda_s = \int_0^{\nu_0} \lambda_s(\bar{\nu}) d\bar{\nu} \sim v^2 \nu_0^2 e^2/c^3 h \left| \int d\tau \bar{\theta}_r \psi_0 \right|^2 . \tag{26}$$

The ratio of this to (20) gives the relative probability that radiation will be emitted in the disintegration:

$$\lambda_s/\lambda_0 \sim e^2/hc \cdot (v/c)^2 \tag{27}$$

in agreement with H. P. (133). From (25) it is clear that only a much more detailed knowledge of θ_r and ψ_0 and of the form of the Hamiltonian H in (16) than is at present available can give us any precise value for λ_s/λ_0.

The application of (27) enables us to estimate the relative probability of radiative and radiationless capture of electrons from atoms by an alpha particle, and gives for the ratio of the probabilities 10^{-6}, in agreement with the more detailed calculations of the effect.

BOUNDARY CONDITIONS AND THE MEANING OF WAVE GROUPS IN WAVE MECHANICS

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Abstract

Reasons are given for believing that the boundary conditions at a discontinuity in the potential (V) in wave mechanics may be $\phi_1=\phi_2\mu^{1/2}$ and $\phi_1 d\phi_1/dx=\phi_2 d\phi_2/dx$. Here ϕ is the wave function and μ the ratio of the group velocities. With these boundary conditions the waves are either completely transmitted or completely reflected according as the energy E is greater or less than V. The particles therefore need not be supposed to enter the region in which $V>E$ where their velocities would be imaginary and their kinetic energies negative. It is suggested that the group of waves associated with a particle should be identified with the particle and that the energy and momentum of the particle are the energy and momentum of the group of waves. When the group is stopped or absorbed it contracts to small dimensions and so becomes a particle.

IN THE applications of wave mechanics to the theory of thermionics and of the disintegration of atomic nuclei the boundary conditions at a discontinuity in the potental have been considered and it is customary to suppose that the wave function ϕ and its first derivative must be continuous at the discontinuity.

Consider the case of a particle with energy E moving along x in the positive direction and suppose that its potential energy is zero for $x<0$ and equal to V' for $x>0$ so that there is a discontinuity in the potential at $x=0$. The usual wave equations in this case are

$$\frac{d^2\phi}{dx^2}+k^2E\phi=0, \qquad x<0$$

$$\frac{d^2\phi}{dx^2}+k^2(E-V')\phi=0, \quad x>0.$$

As a solution we may take, as usual, when $E>V'$,

$$\phi_1=a\epsilon^{-ikE^{1/2}x}+b\epsilon^{ikE^{1/2}x}, \qquad x<0$$

$$\phi_2=c\epsilon^{-ik(E-V')^{1/2}x}, \qquad x>0.$$

To determine b and c in terms of a it is usual to suppose that $\phi_1=\phi_2$ and $d\phi_1/dx=d\phi_2/dx$ at $x=0$. We then get $b=a(1-\mu)/(1+\mu)$ and $c=2a/(1+\mu)$ where $\mu=[(E-V')/E]^{1/2}$ which is equal to v_2/v_1 where v_1 is the group velocity for $x<0$ and v_2 that for $x>0$.

The condition $\phi_1=\phi_2$ at $x=0$ gives $a+b=c$. This equation is not obviously correct. Consider two points A and B one at $x=-d$ and the other at $x=+d$. Since there is a discontinuity in the potential at $x=0$, so that the group velo-

city v_1 for $x<0$ changes to v_2 for $x>0$, it is not clear that the chance that the particle is in an element dx at A should become equal to the chance that it is in a dx at B as d is diminished indefinitely. This is so because A and B are on opposite sides of the discontinuity even when $d=0$.

To determine the correct boundary conditions at $x=0$ we may begin by considering a case in which the potential varies gradually from 0 to V' near $x=0$ and then make the distance in which the change from 0 to V' takes place small.

Let a train of waves moving along x in the positive direction be represented by $\phi=A\epsilon^{-ikB}$ where A and B are functions of x which weshall suppose to be real quantities. ϕ must satisfy the wave equation

$$\frac{d^2\phi}{dx^2}+k^2(E-V)\phi=0$$

where E is the total energy and V the potential energy of the particle. Substituting the above value of ϕ in this equation we get

$$\frac{1}{A}\frac{d^2A}{dx^2}-k^2\left(\frac{dB}{dx}\right)^2-ik\left(\frac{d^2B}{dx^2}+\frac{2}{A}\frac{dA}{dx}\frac{dB}{dx}\right)+k^2(E-V)=0$$

Hence we must have $d^2B/dx^2+(2/A)\,(dB/dx)\,(dA/dx)=0$ which gives $C=A^2dB/dx$[1] where C is a constant. It will be noted that this result is exact not merely an approximation. Also

$$\frac{1}{A}\frac{d^2A}{dx^2}-k^2\frac{c^2}{A^4}+k^2(E-V)=0. \tag{1}$$

Now let $A=A_1+(A_2-A_1)/(\epsilon^{-\alpha x}+1)$ where α is a positive constant. This makes $A=A_2$ where αx is large and positive and $A=A_1$ where αx is large and negative. Thus A changes from A_1 to A_2 in the region near $x=0$ and if we suppose α to become infinite then we shall have $A=A_1$ for $x<0$ and $A=A_2$ for $x>0$.

Substituting this value of A in (1) and putting $c=A_1^2E^{1/2}$ we get

$$V=\frac{\alpha^2(A_2-A_1)(\epsilon^{-\alpha x}-1)\epsilon^{-\alpha x}}{k^2(A_2+A_1\epsilon^{-\alpha x})(1+\epsilon^{-\alpha x})^2}+E\left\{1-\left(\frac{A_1(1+\epsilon^{-\alpha x})}{A_2+A_1\epsilon^{-\alpha x}}\right)^4\right\}.$$

According to this when αx is large and negative then $V=0$ and when αx is large and positive then $V=E\{1-(A_1/A_2)^4\}=V'$.

Thus if α is supposed large this solution of the wave equation gives the variation of A with x when the potential changes rapidly near $x=0$ from the constant value zero when x is negative to the constant value V' when x is positive.

The value of B can be found if desired since $C=A^2dB/dx$ but since $\phi\bar{\phi}=A^2$ it is not required.

Put $\alpha^2=\beta k^2E$ where β is a constant and also let $y=\epsilon^{-\alpha x}$. The expression for V above then becomes in the case when $A_2=2A_1$.

$$V=E\left\{\frac{\beta y(y-1)}{(2+y)(1+y)^2}+1-\left(\frac{1+y}{2+y}\right)^4\right\}$$

[1] An approximate result equivalent to this is well known.

The expression $y(y-1)\ /\ (2+y)\ (1+y)^2$ has a maximum value equal to about 0.08 when $y=3.3$. $\{(1+y)/(2+y)\}^4$ is then about 0.4 so that β may be made equal to 4 without danger of V becoming greater than E. Fig. 1 shows the variation of A with $2k\ E^{1/2}x$ when $A_2=2A_1$ and $\beta=4$. Fig. 2 shows the corresponding variation of V/E with $2k\ E^{1/2}x$ and Fig. 3 shows the variation of V/E with $2\ (2)^{1/2}\ k\ E^{1/2}x$ with $\beta=8$. In Fig. 3 V/E becomes greater than unity.

It appears that, in this case, with $\beta=4$, practically all the changes in A and V takes place in a range of $2kE^{1/2}x$ equal to about 5. Thus if d denotes the thickness of the layer in which the potential changes then we have $d=5/2k\ E^{1/2}$. For electrons $k=4\times10^{13}$ and $E=1.6\times10^{-12}\ P$ where P is the potential difference in volts equivalent to E. Hence $d=5\times10^{-8}/P^{1/2}$. The wave-length λ of the waves associated with an electron is given by $\lambda=12.25/P^{1/2}$ so that $d=0.4\lambda$. Thus if $P=10$ volts then $d=2\times10^{-8}$cm and if $P=1$ volt then $d=5\times10^{-8}$cm. In the case considered V' is equal to $15E/16$. It appears that the potential does not become greater than E in a layer similar to those on the surface of metals for which V' is about 10 volts and d about 5×10^{-8} cm.

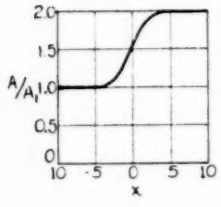

Fig. 1.

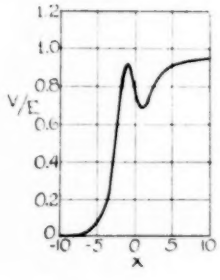

Fig. 2.

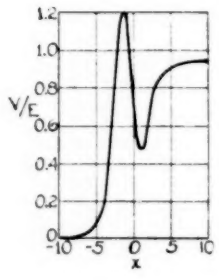

Fig. 3.

When V' is equal to $15E/16$ then the ratio of the group velocities $\mu=v_2/v_1=\frac{1}{4}$ so that $b=a(1-\mu)/(1+\mu)$ is equal to $3a/5$. Hence $b^2a^2=9/25$ so that $9/25$ of the electrons should be reflected back if the boundary conditions $\phi_1=\phi_2$ and $d\phi_1/dx=d\phi_2/dx$ are correct. But as we have just seen when V changes from 0 to $15/16$ of E in a distance of about half a wave-length there is no reflection. This suggests that the boundary conditions should be modified so as to make the reflection zero when $E>V'$.

The equation $V'=E\{1-(A_1/A_2)^4\}$ gives $A_2/A_1=(v_1/v_2)^{1/2}$ or $A_2=A_1\mu^{1/2}$.

For $x<0$ let $\phi_1=a\epsilon^{-ikE^{1/2}x}$ so that $A_1=a$ and $B=E^{1/2}x$. It then follows that for $x>0$ $\phi_2=(a/\mu^{1/2})\epsilon^{-ik(E-V')^{1/2}x}$.

It appears therefore that in the equations

$$\phi_1 = a\epsilon^{-ikE^{1/2}x} + b\epsilon^{+ikE^{1/2}x}$$

$$\phi_2 = c\epsilon^{-ik(E-V')^{1/2}x}$$

we must have $b=0$ and $c=a/\mu^{1/2}$, if there is no reflexion when V' is less than E.

According to this the boundary condition $\phi_1=\phi_2$ at $x=0$ must be replaced by $\phi_1=\phi_2\mu^{1/2}$. The condition $d\phi_1/dx=d\phi_2/dx$ cannot then be correct. Since the number of particles falling on the surface at $x=0$ must be equal to the number leaving it we must have $a^2v_1=b^2v_1+c^2v_2$ or $a^2-b^2=c^2\mu$. The condition $\phi_1=\phi_2\mu^{1/2}$ gives $a+b=c\mu^{1/2}$ so that $a-b=c\mu^{1/2}$. This requires that $\mu^{1/2}d\phi_1/dx$ should be equal to $d\phi_2/dx$ or that $\phi_1 d\phi_1/dx=\phi_2 d\phi_2/dx$. This suggests that the correct boundary conditions at the discontinuity may be $\phi_1=\phi_2\mu^{1/2}$ and $\phi_1 d\phi_1/dx=\phi_2 d\phi_2/dx$. These conditions give $a+b=c\mu^{1/2}$ and $(a+b)(a-b)=c^2\mu$. These equations have two solutions which are $b=0$ and $c=a/\mu^{1/2}$ and $c=0$ and $b=-a$. The first solution as we have seen is the one to use when $E>V'$ so that then $\phi_1=ae^{-ikE^{1/2}x}$, $\phi_2=(a/\mu^{1/2})e^{-ik(E-V')^{1/2}x}$ so that all the particles go through the plane $x=0$ exactly as in classical theory. The other solution is clearly the one to use when $V'>E$ so that then $\phi_1=ae^{-ikE^{1/2}x}-ae^{ikE^{1/2}x}$, $\phi_2=0$ so that all the particles are reflected back at $x=0$ exactly as in classical theory.

Thus if the boundary conditions at a discontinuity are $\phi_1=\phi_2\mu^{1/2}$ and $\phi_1 d\phi_1/dx=\phi_2 d\phi_2/dx$ then when $V'>E$ the waves are reflected completely at the discontinuity so that the particles need not be supposed ever to enter the region in which $V'>E$ where their kinetic energy is negative. This seems to the writer to be a very strong argument in favor of these boundary conditions.[2] It is very difficult to imagine any sort of physical meaning which can be attached to the idea of a particle with an imaginary velocity and a negative kinetic energy.

The writer now proposes to bring forward some considerations with regard to the nature of wave groups in wave mechanics. The view proposed is perhaps unorthodox and may not meet with approval but it seems to the writer to be worth considering.

It was originally suggested by Schroedinger that the wave function ϕ could be interpreted by supposing that the density of the electricity is proportional to $\phi\bar{\phi}$. This view has been replaced, at least in many cases, by the idea that the chance that an electron is in an element of volume dv is proportional to $\phi\bar{\phi}\,dv$. According to the original idea the electron in standing waves was at rest but was spread out over the whole volume occupied by the waves. A moving electron was spread out over a moving group of waves. According to the later view the electron is presumably somewhere in the standing waves or group but its location and motion, if any, are unknown. According to the first view the electron when it appears somewhere as a minute particle must have contracted from its state of diffusion over the waves. This necessary contraction seems to me to be of fundamental importance, as will be explained below.

Although according to the present view the motion of an electron in standing waves cannot be determined it seems to the writer to be nevertheless allowable to suppose that it must move from one point to another,

[2] Nordheim (Proc. Roy. Soc. A December 3, 1928) concludes that practically all the electrons having $E>V'$ escape from a metal because of the effect of the image forces in rounding off the discontinuity.

when it does move, along some definite path. That is, it will not do to suppose that it disappears at one point and appears at another without occupying the intermediate positions.

Another possible view, very similar to Schroedinger's original suggestion, is that the group of waves and the electron are identical and that when the group is stopped or absorbed and appears at a point the group of waves contracts to small dimensions and so becomes a particle.

If we suppose that a particle is associated with or is a group of waves of length l then it is easy to show that l diminishes when the velocity v of the group diminishes. This idea is not new but it does not seem to have attracted much attention.

According to Heisenberg's uncertainty principle we have $\delta E \delta t = h$, roughly at least, where δE is the uncertainty in the energy of the particle and δt that in its time of passing a given point. If v is the group velocity then we have $\delta t = l/v$ and since $E = h\nu$ where ν is the frequency of the waves we get $l = v/\delta\nu$[3] where $\delta\nu$ is the uncertainty in the frequency ν. There seems to be no reason to suppose that δE or $\delta\nu$ should vary as the group moves along so that we may conclude that the group length l should be approximately proportional to the group velocity v. Thus if the group enters a field of force in which it is gradually slowed down we should expect l to become smaller and to become very small on a surface where the group velocity is zero. It does not become zero at this point because owing to the uncertainty in E there is some uncertainty in the position of the surface in question.

Darwin's solution[4] of the motion of a group in a uniform force field does not indicate such a variation of l which must mean that his solution involves a variation of $\delta\nu$ with v so that $v/\delta\nu$ remains constant or rather only varies to the extent demanded by the uncertainty in v. It seems to the writer that $\delta\nu$ should be supposed constant and so l should vary with v. Thus when a group is brought to rest it becomes very small or we may say that it becomes a particle. If preferred we may say that the group contracts onto the particle in it which is so located in a nearly definite position when the group stops. According to this we should expect the group and particle to come to rest approximately on a surface at which $E - V = 0$ and so either to remain on such a surface or else to move back into the region where $E > V$. We should not expect the particle to penetrate into the region where $V > E$ where its kinetic energy would be negative. It seems to the writer that this is as it should be. When a mathematical theory indicates that particles if in a certain region would have imaginary velocities and negative kinetic energies then the proper conclusion to draw is that the particles do not go into that region. Of course when there is uncertainty in E then the position of the surface $E - V = 0$ is subject to a corresponding uncertainty. This conclusion is supported by the results obtained above on the motion of electrons through a discontinuity or near discontinuity in the

[3] This result is given by H. T. Flint, Proc. Roy. Soc. A, December 2, 1929.

[4] Darwin, Proc. Roy. Soc. A, December 1, 1927.

potential. The electrons and the waves also are probably reflected unless $E > V'$.

Bridgman's suggestion that the negative sign on the kinetic energy of particles inside the region where $V > E$ is merely the "bar sinister" on particles which have got in improperly is similar to Rutherford's suggestion that particles somehow leak through a potential hump although they have not got enough energy to get over it. In my opinion it is better to suppose that they do not get into regions where $V > E$ in any case.

It seems worth while to point out that the conclusion that particles can enter regions in which $V > E$ may be due to the assumption that the energy E can have a definite value with zero uncertainty. It seems probable that there should always be some uncertainty in E so that any one particular solution of the wave equation $\Delta\phi + k^2(E-V)\phi = 0$ for an exact value of E does not really represent a possible state of things. Such solutions correspond to a group of waves of infinite length, since $l = hv/\delta E$, and if the group is really of finite length then they are merely approximations. When the region occupied by the waves is of atomic dimensions the group may be long enough to overlap itself many times and so the solution for a group of infinite length is a good approximation. But there should be some uncertainty in E so that the particle may have enough energy to go through the surface $E - V = 0$ of the approximate solution[5] without its kinetic energy becoming negative.

Consider the case of an electron moving normally between two parallel plane surfaces at which it is reflected back. As in the theory of the discontinuity with $V' > E$, if we suppose the group length to be infinite, we may take $\phi\bar{\phi} = 4a^2 \sin^2 kE^{1/2}x$. Thus we have nodal planes half a wave-length apart on which $\phi\bar{\phi} = 0$. The distance between the parallel reflectors must be a multiple of the half wave-length. The chance that the electron is between any pair of adjacent planes is then $\lambda/2\ d$ where d is the distance between the reflectors. We do not know where the electron is but it is supposed to be moving backwards and forwards between the reflectors with uniform velocity v. It is therefore supposed to pass through the nodal planes one after another. But on these planes $\phi\bar{\phi} = 0$ so that the chance that the electron is at any nodal plane is zero. It cannot therefore be supposed to be moving with uniform velocity and so passing through the nodal planes.[6] We may if we like suppose a large number of electrons present all having the same energy and so all having nodal planes in the same positions.

Wiener's experiments on standing light waves may be considered in this connection. The particles are then photons instead of electrons. He showed by means of a thin photographic film that there were nodal planes half a wave-length apart at which the film was unaffected. If the photons were moving towards and away from the mirror they would pass through the

[5] The exact solution, of course, would be the sum of a number of the solutions for particular values of E each multiplied by a suitable factor.

[6] The argument here is directed against the *assumption* that the electron is moving with uniform velocity v.

film whatever its distance from the mirror and so the film would be equally affected at any distance. The fact that the film is affected between the nodal planes shows that the photons get there but the fact that it is not affected on the nodal planes shows that the photons do not pass through the nodal planes.

In the opinion of the writer, if the idea that a group of waves contains a particle is retained, then these considerations about standing waves make it necessary to suppose that in standing waves the particle is at rest. This amounts to a partial return to Schroedinger's original idea. In the case of a large number of particles being reflected normally we must suppose that they are arranged in layers between the nodal planes. The way in which such an arrangement could be brought about can be easily imagined.

Consider a group of waves of length l containing one particle[7] and suppose that the particle is at a distance d from the front of the group. If the group is reflected normally the reflected waves will meet the particle when it is at a distance $d/2$ from the mirror. The particle will then stop since it is in standing waves and it will remain stopped for a time $(l-d)/v$ and will then move away with the reflected waves. According to this the waves must convey the momentum $2mv$ which the particle loses to the mirror. It is therefore necessary to suppose that the waves of wave mechanics are not merely waves of probability but that they are real physical waves which can convey energy and momentum. In fact it would seem to be best to regard the energy and momentum of a particle as the energy and momentum of its group of waves. When the group is stopped the energy and momentum appear on the particle or the group becomes a particle.

It will be observed that according to this when a particle is reflected back at a discontinuity in the potential in which $V'>E$ the particle does not get to the discontinuity at all unless it happens to be exactly at the front of its group of waves.[8] Hence even if we suppose that the waves do penetrate through the discontinuity with amplitude falling off exponentially on the other side the particle need not be supposed ever to go through. For example we might suppose that the particle is always located at the crest of a wave and so is never exactly at the front of the group.

To represent a moving particle it is necessary to have a moving group of waves. Standing waves do not represent moving particles. Any solution of the equation $\Delta\phi+k^2(E-V)\phi=0$ which represents standing waves may be said to be a group of waves at rest. For example when an electron is captured by a proton the group of the electron may be said to form the waves of the resulting hydrogen atom. The electron group contracts to atomic dimensions in this case. The electron group is of finite length and so must have uncertainty in its energy which should persist in the energy of the atom formed.

[7] Particle here may mean either electron or photon. The groups associated with photons are of finite length which indicates uncertainty in the frequency and energy just as for electrons.

[8] The particle is supposed to be somewhere in its group. To assume that it is at a distance d from the front of the group does not involve the assumption that d can be determined experimentally.

The standing waves may be said to be the particle but if it is desired to suppose that there is a particle somewhere in the standing waves then since it should be at rest it seems natural to suppose that it is on the surface $E-V=0$ or else in a region where V is constant. If the particle remains at rest on the surface $E-V=0$ or anywhere in a field of force it cannot be supposed to be acted on by the field of force. It is therefore necessary to suppose that fields of force do not act directly on the particles but merely alter the wave velocity. This of course is implied by the accepted method in wave mechanics which is to calculate the effect of the force field on the waves and not on the particles.

According to what has been said above the waves should not be supposed to go into the regions where $V>E$ but should be reflected at the surface $E-V=0$ or else it should be supposed that $\phi\bar{\phi}dv$ is only proportional to the probability that a particle is in dv when $E\geqq V$ at dv. The integral $\int\phi\bar{\phi}dv$ should in this case be made equal to unity when taken only over the region in which $E\geqq V$. A third alternative which seems to the writer very plausible is to suppose that the energy E has enough uncertainty in its value to account for the chance that the particle may be in the region where $V>E$. That is we suppose $E=E_0\pm\delta E$ and if a particle is found where $V>E_0$ then δE is equal to $V-E_0$ at least.

The second or third alternatives seem at the moment to be the more acceptable but it may be worth while to mention that the energy levels of the hydrogen atom may be very simply obtained by supposing that spherical waves are reflected at the surface $E-V=0$ and so form standing waves.

Since in the hydrogen atom the wave velocity is equal to $E/(2m(E+e^2/r))^{1/2}$ the time T required for spherical waves to move from the nucleus to a sphere of radius $-e^2/E$ and back is given by

$$T=2\int_0^{-e^2/E}\frac{[2m(E+e^2/r)]^{1/2}}{E}dr=-\frac{\pi e^2}{E}\left(\frac{2m}{-E}\right)^{1/2}.$$

We may suppose that $T=n/\nu$ where ν is the frequency of the standing waves and n is an integer and that $E=-h\nu$ so that $E=-2\pi^2me^4/n^2h^2$ as usual.

One of the difficulties in optical theory is to see how the energy and momentum of the waves can become concentrated at points when the light is absorbed. The view that the waves have no energy or momentum is not satisfactory because for example it is difficult to see how waves with no energy could be reflected by a mirror. Reflexion requires the electrons all over the surface of the mirror to oscillate with the frequency of the light. The hypothesis of virtual oscillators in the mirror is also very unsatisfactory. A similar difficulty is present in the wave theory of electrons. The waves are diffracted as though they had uniformly distributed energy but appear as electrons when absorbed. According to what has been said above this difficulty may be to some extent removed by supposing that the wave groups contract to small dimensions when stopped. This process of contraction is made possible by the increase in the wave velocity as the group velocity

diminishes. The wave velocity becomes infinite when the group velocity becomes zero so that the group can contract very rapidly as it stops. It seems reasonable to suppose that the same thing happens with light as with electrons. When light is moving in empty space the wave and group velocities are equal but in the intense fields inside atoms we may suppose that the group velocity is diminished and the wave velocity increased. It is nevertheless very difficult to imagine a group occupying many cubic feet to be absorbed by an electron. If it is supposed that when the photon in a group is slowed down the wave velocity all over the group becomes very large and infinite when the photon stops then it is possible to imagine a very large group to contract very rapidly onto the photon. Even if we admit such sudden group contractions to be possible great difficulties remain. For example we have to explain why some groups are reflected and others not and how a group can be reflected without giving up any energy to the mirror.

As we have seen above a group of waves associated with a particle of energy E is either completely transmitted or completely reflected at a discontinuity in the potential according as $E>V'$ or $E<V'$. This suggests that the group associated with a photon must be either completely transmitted or completely reflected by a mirror. If the energy and momentum of photons and electrons are in the wave groups associated with them then it is necessary to suppose that these groups never divide into two and so must be either completely reflected or completely absorbed. In the case of photons exceptions to this may be supposed possible since a single photon may be imagined to give rise to two or more photons having the same total energy as the original one. The classical theory of reflexion must then be supposed to give the probability that a wave group and its photon are reflected together and not merely the chance that the photon is reflected.

The view suggested is therefore that a particle such as a photon or electron is practically identical with the group of waves associated with it. The energy and momentum are spread out over the group and not concentrated at a point. When the group is stopped or absorbed it contracts to small dimensions and so becomes a particle. The group cannot be divided by reflexion or by passing through a small aperture in an opaque screen but must be either all stopped or all get through. The group of waves must be regarded as a material entity and wave theory must be regarded as an approximation in so far as it now seems to require wave groups to be divided by reflexion and other similar processes which do not involve any change of frequency.

The writer does not claim to have removed the difficulties in optical and mechanical wave theory but he hopes that the above discussion may help to make the serious nature of these difficulties clearer.

THE HEAT OF DISSOCIATION OF CARBON MONOXIDE

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Abstract

The author's method for calculating the heat of dissociation of nitrogen, has now been applied to carbon monoxide. For both N_2 and CO the method agrees with the best values obtained by other methods. Using the present value of 10.3 volts for the heat of dissociation of CO, the dissociation products of the molecule are discussed for several electronic levels. In this way it is shown that the recent value of 1.3 volts for the energy of the metastable $^1D_2$ state in oxygen, obtained by McLennan and Crawford, agrees best with the present work.

IN A short paper that appeared last March,[1] the writer has calculated the heat of dissociation of nitrogen and found it to be equal to 9.0 volts. In a paper on the determination of heats of dissociation by means of band spectra, Professor R. T. Birge[2] has called attention to the difficulty of determining definitely the most probable value of D for N_2. At the same time however he has given what is in his opinion the best value of the heat of dissociation of N_2 and that value is 9.1 volts. Since the method used by the writer yielded a value which is in such good agreement with the one given by Birge, it will be of some interest to try the same method for some other molecule. One of the cases that is of immediate interest is that of carbon monoxide.

It is now generally recognized that the bands of the third positive group of carbon arise in transitions from the b to the a level, and that only the $v'=0$ progression has been observed.[3] The same reason for the non-appearance of higher progressions can be given here as was given for the fourth positive group of nitrogen. If the value of $\omega_0 x$ for the b level of CO is very large, then the heat of dissocation in that level will be very small and dissociation will occur when the total energy of the molecule in the b level is only slightly greater than its electronic energy. It may be that $\omega_0 x$ is of such a magnitude that not even a single discrete vibrational state exists, in which the total energy of the molecule is less than the heat of dissociation.

If one uses the above reasoning as a basis, it is then possible to determine the heat of dissociation, since the products of dissociation from the b level have been theoretically predicted to be a normal carbon atom and a normal oxygen atom.[4] It immediately follows that the heat of dissociation of CO is either equal to or only slightly greater than the electronic energy in the b level. This energy is equal to 10.35 volts, so that the heat of dissociation of CO must

[1] Kaplan, Proc. Nat. Acad. Sci. **15,** 226 (1929).
[2] Birge, Trans. Farad. Soc. in press.
[3] Birge and Sponer, Phys. Rev. **28,** 259 (1926).
[4] R. C. Johnson, Trans. Farad. Soc. **15,** 649 (1929).

be almost equal to 10.35 volts. It is interesting here to remark that the value given by Birge in his Faraday Transactions paper is equal to 10.3 volts. The agreement between the present method and the method used by Birge is extremely satisfactory. The fact, that the fourth positive group of N_2 and the third positive bands of CO are the two outstanding examples of bands for which there is only one v' progression, certainly indicates that the present explanation is worth consideration.

The new value of D will now be applied to a brief discussion of some recent ideas regarding carbon monoxide. Johnson has given a very extensive discussion of the carbon monoxide molecule in his Faraday Society paper, and in particular he has discussed tentatively the dissociation products from the various electronic states of the molecule.

If the present value of 10.3 volts is to be accepted then it follows that at least one of the dissociation products from the electronic states that lie above 10.3 volts, must be in an excited state. Using the formerly accepted value of 11.2 volts for D, Johnson has already made the above statement for the c level. In view of the present lower value for D, the same statement must now apply to the b' level, the dissociation products of which were predicted to be a normal carbon and a normal oxygen atom.

One of the most interesting levels, from the point of view of the ideas presented in this paper, is the F level. The value of ν_e for this level is 99,730 cm^{-1} and ω_0 and $\omega_0 x$ are 1914 cm^{-1} and 198 cm^{-1}, respectively. The F level is thus an example of a molecular level having a very high value for $\omega_0 x$, as compared with the values of $\omega_0 x$ for nearly all of the known molecular levels. Because of the large $\omega_0 x$, a linear extrapolation of the vibrational levels, associated with the F level, yields a small and probably a fairly accurate heat of dissociation. The heat of dissociation is equal to 0.57 volts and the total energy in the F level is 12.88 volts. The difference between this and the heat of dissociation yields 2.5 volts as the energy of the two products of dissociation. Since the products of dissociation from this level are predicted to be a $^1D_2$ carbon atom and a $^1D_2$ oxygen atom, the sum of the energies of $^1D_2$ in carbon and in oxygen must be equal to 2.5 volts and this is probably a fairly good estimate of the sum.

One other state that possesses a fairly high value of $\omega_0 x$ is the B level and a linear extrapolation yields a value of 2.8 volts as the heat of dissociation for this level and a value of 3.2 volts for the energy of the dissociation products. This extrapolation is longer than the one for the F level and is undoubtedly less trustworthy, probably being too high. Once again the products of dissociation are predicted to be a ^1D carbon and a ^1D oxygen atom, so that if the assumption is made that the error in the extrapolation is about 25 percent then the lower value is not far from being correct. A 25 percent error in a linear extrapolation of the above magnitude is not unusual in the determination of heats of dissociation from band spectra.

Two values for the difference $^3P - ^1D_2$ in oxygen have been suggested. One of these is about 1.95 volts, suggested independently by L. A. Sommer[5]

[5] L. A. Sommer, Zeits. f. Physik **51**, 451 (1928).

and the author,[6] and the other is 1.3 volts, obtained by McLennan and Crawford.[7] It is difficult, in view of the theoretical predictions regarding the F level, to accept the higher of the two values, because then the difference $^3P-{}^1D_2$ in carbon would have to be only about 0.6 volts. A comparison of carbon with the spectroscopically similar atoms N^+ and O^{++}[8] makes such a low value highly improbable. On the other hand the 1.3 volt value of McLennan and Crawford is a very reasonable one, since that would make the ^1D level of carbon possess a value of about 1.2 volts and this is much more reasonable than the lower one of 0.6 volts.

The main purpose of this paper has been to point out the fact that the assumption, that the b level is extremely anharmonic, yields a very good value for D. Consequently a more detailed discussion of evidence regarding the energy in the $^1D_2$ state of the oxygen atom would be out of place here and will be left for another communication.

[6] Kaplan, Phys. Rev. **33,** 638 (1929).
[7] McLennan and Crawford, Nature **124,** 874 (1929).
[8] Bowen, Astrophys. J. **67,** 1 (1928).

THE BAND SPECTRUM OF SILVER CHLORIDE

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Abstract

Analysis of vibrational structure. —The electronic band system of AgCl extending from λ3124 to λ3400 has been obtained in emission and absorption, the latter under high dispersion. A complete vibrational quantum analysis has been carried out, giving the following formula for the heads of the bands of the molecule $Ag^{107}Cl^{35}$:

$$\nu = 31574.4 + 275.0v' - 6.20v'^2 - 0.133v'^3 - 342.4v'' + 1.163v''^2.$$

The data give $\omega_e'' = 343.6$ cm^{-1}, $\omega_e' = 281.0$, and $\nu_e = 31606.9$ cm^{-1}. Vibrational quantum numbers have been assigned to Franck and Kuhn's data for AgBr and AgI.

Isotope effects. —The vibrational isotope effect was observed for both the Cl and the Ag atoms. The complete spectrum consists of four overlapping systems due to the four possible isotopic molecules. The order of magnitude of the isotope shift for the Cl isotope effect was 1 to 30 cm^{-1}; for the Ag isotope effect, 1 to 4 cm^{-1}. The agreement of observed shifts with those calculated from the equations recently derived by Birge (not yet published) is close.

Energies and products of dissociation. The heats of dissociation of the AgCl molecule are $D_0'' = 3.11$ volts in the normal state, $D_0' = 0.31$ volt in the excited state. The energy of excitation of the atoms resulting by dissociation from the excited state is 1.10 ± 0.12 volt. This value can be explained if it is assumed that $^2D'$ states exist in Ag as in Cu and Au. It is concluded that the silver halides dissociate from the excited state into a silver atom in a $^2D'$ state and a halogen atom in the metastable $^2P_{1/2}$ state.

Introduction

THE spectrum of silver chloride vapor consists of a system of single-headed bands in the ultra-violet, all the bands being shaded toward the red. These bands were first obtained by Franck and Kuhn[1] in absorption and fluorescence. Their work was concerned chiefly with a study of the type of molecular binding of the silver halides AgI, AgBr, and AgCl. Their results indicate that these molecules are of the "atom-molecule" type, in contrast to the alkali halide "ion-molecule" type. AgCl gave only a discontinuous band spectrum, whereas AgBr and AgI each showed a single continuous spectrum in addition to bands. The heats of dissociation of AgI and AgBr were calculated from the long wave-length limit of the continuous spectrum assuming that the product of dissociation from the excited state were a normal silver atom and an excited halogen atom. The heats of dissociation were also found independently by extrapolation of the fluorescence series. But for AgCl no direct calculation was possible by either method. The authors were not able to assign vibrational quantum numbers for any of these band systems. No mention was made of an isotope effect.

[1] Franck and Kuhn, Zeits. f. Physik, **43**, 164 (1927); **44**, 607 (1927).

In the present research, a complete vibrational quantum analysis of the AgCl band spectrum has been made. Accurate determinations of the heats of dissociation of the molecule in both the normal and the excited states lead to new conclusions as to the products of dissociation of the silver halides. In addition, the vibrational isotope effect of both atoms simultaneously has been obtained.[2] This is the first time the silver isotope effect has been obtained in spectra.

Emission Spectrum

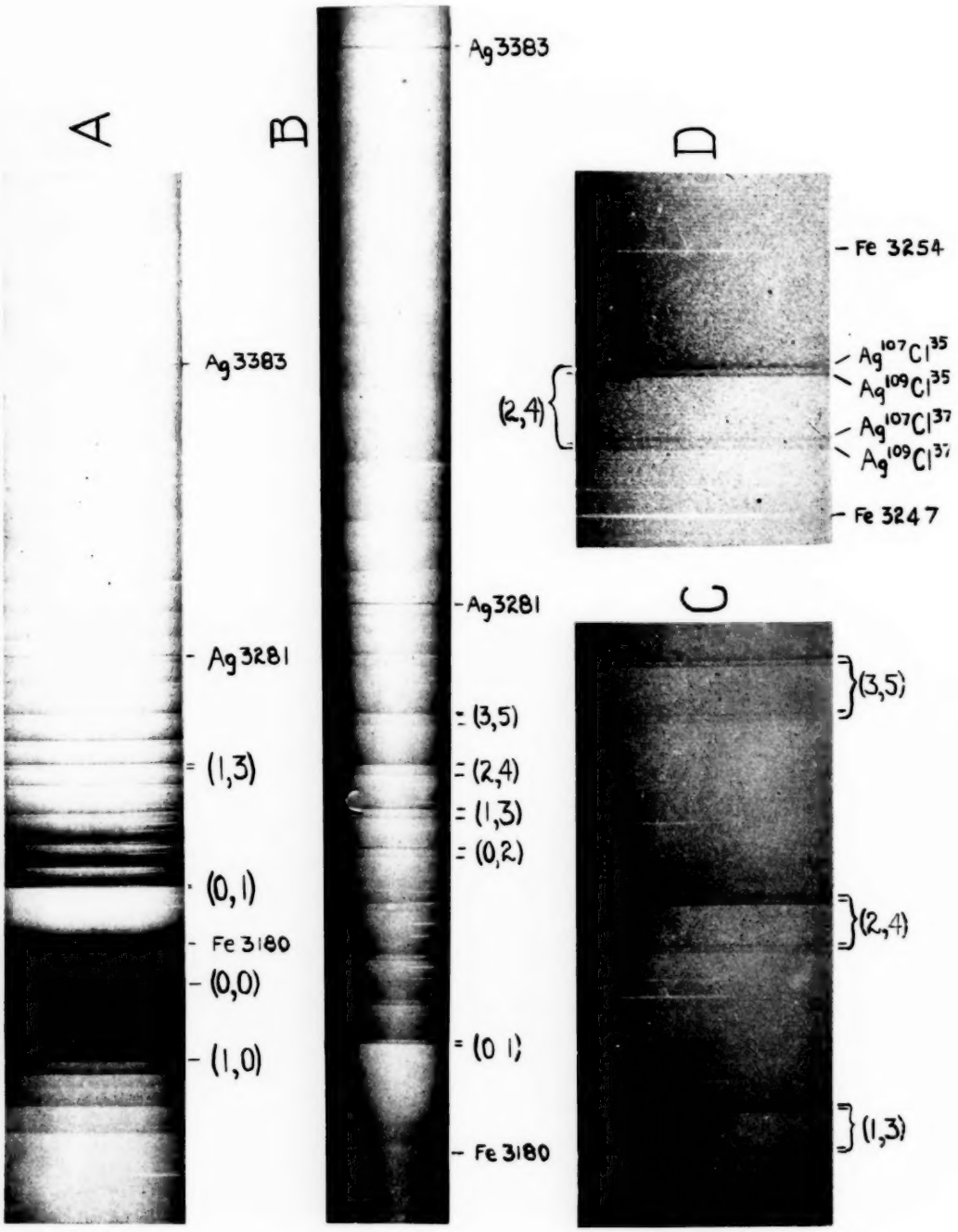
The silver chloride band spectrum was obtained in emission[3] by viewing the region immediately above a long silver electrode covered with fused AgCl, in a high voltage discharge in hydrogen at about 1 mm pressure. Photographs were made with a quartz Hilger E2 spectrograph. The small number of bands appearing in emission permitted a ready assignment of vibrational quantum numbers. The heads of the following bands were obtained in emission: (0, 0), (1, 0), (0, 1), (1, 1), (2, 1), (1, 2), (3, 2), (2, 3), (3, 4). Of the bands recorded by Franck and Kuhn, those which do not fit into this assignment can be shown to belong to the fainter isotope molecule $AgCl^{37}$. In order to extend the observations of the isotope effect and to obtain accurate values for

TABLE I. *Wave-lengths and wave-numbers of observed heads. F. & K., bands observed by Franck and Kuhn.*

	$Ag^{107}Cl^{35}$		$Ag^{109}Cl^{35}$		$Ag^{107}Cl^{37}$		$Ag^{109}Cl^{37}$		F. & K.
(v', v'')	λ	ν	λ	ν	λ	ν	λ	ν	ν
(2, 0)	—	—	—	—	3114.60	32077.0	—	—	32096
(3, 1)	3124.17	31999.3	—	—	3124.79	31992.9	—	—	32005
(4, 2)	3135.10	31887.7	—	—	3135.39	31884.7	—	—	—
(1, 0)	3139.70	31841.0	—	—	3140.15	31836.4	—	—	31845
(2, 1)	3147.93	31757.7	—	—	—	—	—	—	31760
(3, 2)	3157.48	31661.7	—	—	—	—	—	—	31663
(0, 0)	3166.21	31574.4	—	—	—	—	—	—	31579
(1, 1)	3173.35	31503.4	—	—	3173.60	31500.9	—	—	31506
(2, 2)	3181.95	31418.2	—	—	3181.59	31421.8	—	—	31426 *i*
(0, 1)	3200.81	31233.1	—	—	3200.07	31240.3	—	—	31243 *i*
(1, 2)	3208.03	31162.8	—	—	3207.14	31171.4	—	—	31174 *i*
(2, 3)	3216.26	31083.0	—	—	3215.28	31092.5	3215.16	31093.7	31094 *i*
(3, 4)	3225.79	30991.2	—	—	3224.46	31004.0	—	—	30998
(0, 2)	3235.98	30893.7	3235.82	30895.2	3234.50	30907.8	3234.31	30909.6	30908 *i*
(1, 3)	3243.18	30825.0	3242.97	30827.0	3241.50	30841.0	3241.31	30842.8	30833
(2, 4)	3251.35	30747.6	3251.14	30749.6	3249.47	30765.4	3249.24	30767.6	30755
(3, 5)	3260.77	30658.8	3260.52	30661.2	3258.63	30678.9	3258.35	30681.5	30667, 30687
(4, 6)	3271.76	30555.8	3271.46	30558.6	3269.26	30579.2	3268.98	30581.8	30564
(1, 4)	3278.63	30491.8	3278.33	30494.6	3276.23	30514.1	3275.91	30517.1	30495
(2, 5)	3286.77	30416.3	3286.48	30418.9	3284.15	30440.5	3283.87	30443.1	30422
(3, 6)	3296.20	30329.3	3295.87	30332.3	3293.30	30356.0	3292.94	30359.3	30335, 30356
(4, 7)	3307.14	30228.9	3306.82	30231.8	3303.91	30258.5	3303.49	30262.3	30235, 30262
(2, 6)	3322.77	30086.7	3322.42	30089.9	—	—	—	—	—
(3, 7)	3332.14	30002.1	3231.73	30005.8	—	—	—	—	30008
(4, 8)	3343.11	29903.7	3342.70	29907.4	—	—	—	—	29912
(4, 9)	3379.55	29581.2	3379.10	29585.2	—	—	—	—	29590
(5, 7)	—	—	—	—	—	—	—	—	30443
(5, 8)	—	—	—	—	—	—	—	—	30118
(5, 9)	—	—	—	—	—	—	—	—	29795
(6, 10)	—	—	—	—	—	—	—	—	29655
(3, 8)	—	—	—	—	—	—	—	—	29689
(5, 10)	—	—	—	—	—	—	—	—	29475
(6, 11)	—	—	—	—	—	—	—	—	29327
(4, 10)	—	—	—	—	—	—	—	—	29270
(5, 11)	—	—	—	—	—	—	—	—	29161
(6, 12)	—	—	—	—	—	—	—	—	29014
(5, 12)	—	—	—	—	—	—	—	—	28839
(6, 13)	—	—	—	—	—	—	—	—	28694

[2] B. A. Brice, Phys. Rev. **34,** 1227 (1929) (Letter).

[3] B. A. Brice, Phys. Rev. **33,** 1090 (1929) (Abstract).



SILVER CHLORIDE ABSORPTION

Fig. 1.

the heats of dissociation, it was considered worth while to photograph AgCl vapor in absorption under high dispersion.

Absorption Spectrum

The absorption spectrum was obtained by passing white light from a tungsten quartz lamp through AgCl vapor. The salt was heated to about 900°C in an open quartz tube 2 ft long surrounded by an electric furnace. Photographs were taken using a 21 ft concave grating, giving a dispersion of 2.5 A/mm in the first order and 1.3 A/mm in the second order. The grating* is mounted according to Paschen in a temperature-controlled room. The photographs are reproduced in the accompanying plate. Photograph *A* shows the first order spectrum, *B* the second order; the enlargements *C* and *D* illustrate in more detail the isotope effect, showing the four heads composing each band. The comparison spectrum is that of an iron arc, the standard wave-lengths being taken from Kayser's Handbuch Vol. VII.

Table I gives the wave-lengths in air of the observed heads. The corresponding wave-numbers are corrected to vacuum by using Kayser's table. The values recorded are the mean of two independent measurements on a first order plate and one on a second order plate. The heads given by Franck and Kuhn are also recorded for comparison. It is evident that their measurements are from 3 to 10 cm^{-1} too high.

Vibrational Analysis

Throughout this paper the notation used will be as far as possible consistent with that proposed recently by Mulliken for the general theory of band spectra, and that proposed by Birge[4] for the isotope theory. The *true* vibrational quantum number is integral, $v=0, 1, 2, \cdots$; the *effective* quantum number is half-integral, $u=v+\frac{1}{2}$. Subscripts e refer to the vibrationless but impossible state for which $u=0$; subscripts 0 refer to the lowest possible vibrational state, for which $u=1/2$.

The possible energy levels of a non-rotating molecule are given by

$$G_u = \omega_e(u - x_e u^2 + y_e u^3 + \cdots) \tag{1}$$

where ω_e is the mechanical vibration frequency for vanishingly small amplitude. The wave-numbers of the origins of the bands in the spectrum are

$$\nu = \nu_e + \omega_e'(u' - x_e' u'^2 + y_e u'^3 + \cdots) - \omega_e''(u'' - x_e'' u''^2 + y_e'' u''^3 + \cdots) \tag{2}$$

where ν_e corresponds to the electronic energy change, and is defined as the origin of the band system. The classical vibration frequency is obtained from Eq. (1) by differentiation: $\omega_u = dG_u/du$. But experiment yields values of $\omega_{u+1/2}$, which is the spacing of the energy levels. From Eq. (1)

$$\omega_{u+1/2} = G_{u+1} - G_u = \omega_e u[1 - 2x_e(u + \tfrac{1}{2}) + 3y_e(u + \tfrac{1}{2})^2 + \cdots] \tag{3}$$

* The Anderson grating used at present in this mounting is the property of Townsend Harris Hall, College of the City of New York.

[4] R. T. Birge, unpublished work.

If the data are sufficient, a plot of the observed spacings $\omega_{u+1/2}$ against $u+\frac{1}{2}$ can be used to determine the constants of Eq. (2). The value of ω_u for any value of u can then be obtained from the resulting curve by interpolation or extrapolation. Eq. (2) will then represent the origins (or heads, in practice) of the observed bands.

It is found experimentally that for non-polar molecules the ω_u:u curve is linear for low values of u, and that extrapolation of the linear part to $u=u_0$ when $\omega_u=0$ leads to a fairly reliable determination of the heat of dissociation.[5] This gives $u_0=\omega_e/2x_e\omega_e$. Geometrically the heat of dissociation is given by the area under the ω_u:u curve:

$$D_e=\int_0^{u_0}\omega_u du=\frac{1}{2}\,\frac{\omega_e^2}{2x_e\omega_e} \qquad D_0=\int_{1/2}^{u_0}\omega_u du=\frac{1}{2}\,\frac{\omega_0^2}{2x_e\omega_e} \quad (5),\ (6)$$

Eq. (5) gives the heat of dissociation referred to the equilibrium state. Eq. (6) is the *true* heat of dissociation, referred to the lowest possible vibrational state. There will be a value D_0'' for dissociation by vibration from the normal state, and a value D_0' for the excited state.

Fig. 2 shows the observed heads of the most abundant molecule $Ag^{107}Cl^{35}$ arranged in the customary array which determines the true assignment of vibrational quantum numbers, and which yields the experimental values of $\omega_{u+1/2}''$ and $\omega_{u+1/2}'$. The intensity distribution here is characteristic of molecules having a small change in moment of inertia on electronic transition.

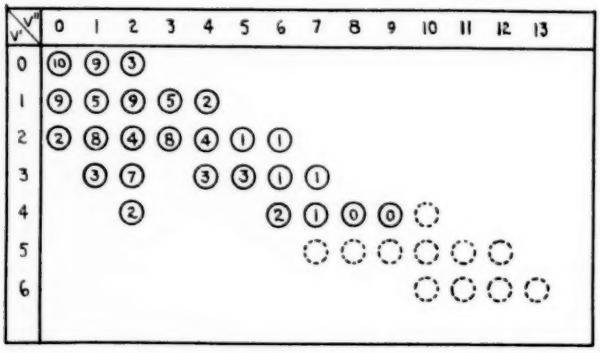


Fig. 2. Assignment of vibrational quantum numbers. Numerals indicate estimated intensities. Dotted circles are additional bands observed by Franck and Kuhn.

Table II contains the values of ω_u for corresponding u, including both the experimental, and the extrapolated and interpolated values, which are needed later for calculating the isotope shifts. In Fig. 3 the ω_u:u curves for the most abundant molecule are A'', A'. The curve A' for the excited state is not a straight line.

[5] Birge and Sponer, Phys. Rev. **28,** 259 (1926). See also Bull. Natl. Res. Council, No. 57 (1926), p. 131; R. T. Birge, Trans. Far. Soc. **25,** 707 (1929).

TABLE II. *Values of* ω_u.

	$Ag^{107}Cl^{35}$		$Ag^{109}Cl^{35}$		$Ag^{107}Cl^{37}$		$Ag^{109}Cl^{37}$	
u	ω_u''	ω_u'	ω_u''	ω_u'	ω_u''	ω_u'	ω_u''	ω_u'
0	343.6	281.0	342.4	—	336.0	276	—	
½	342.4	275.0	341.3	275	334.9	270	—	
1	341.3	268.3	—	—	—	263.6	—	
1½	340.2	262	339.0	262	332.7	257	—	
2	339.0	255.1	—	255.0	332.5	251.1	—	250.7
2½	337.8	249	336.8	249	330.5	245	—	—
3	336.5	242.8	—	242.4	329.9	238.5	—	238.4
3½	335.5	235	334.5	235	328.3	231.3	—	—
4	334.3	226.4	332.4	226.2	327.0	223.2	325.9	222.5
4½	333.2	217	332.2	217	326.2	214	—	—
5	331.9	206 ?	330.7	—	325.0		324.5	
5½	330.8	194 ?	330.0	194	324.0		—	
6	329.6	173 ?	328.9		322.9		322.2	
6½	328.5		327.8		321.8		—	
7	327.1		326.7		320.7		319.5	
7½	326.2		325.6		319.6			
8	325.2		324.4		—			
8½	323.8		323.3		317.4			
9	322.5		322.2					
9½	321.5							
10½	319.2							
11½	316.8							
12½	314.5							

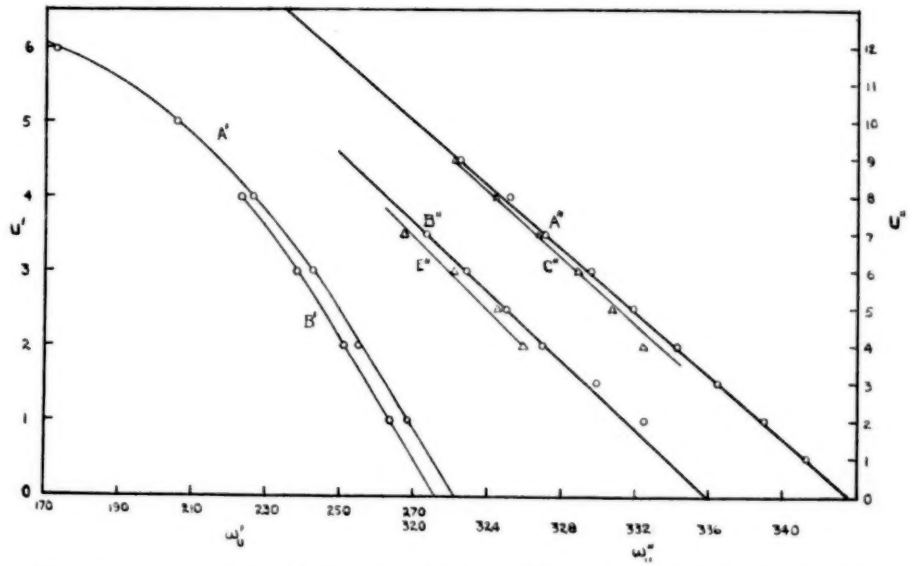


Fig. 3. ω_u: u curves: A'' normal, A' excited state of $Ag^{107}Cl^{35}$; B'' normal, B' excited state of $Ag^{107}Cl^{37}$; C'' normal state of $Ag^{109}Cl^{35}$; E'' normal state of $Ag^{109}Cl^{37}$.

The equation representing the heads of the bands for the molecule $Ag^{107}Cl^{35}$, from Eq. (2) and the above data is:

$$\nu = 31574.4 + 275.0v' - 6.20v'^2 - 0.133v'^3 - 342.4v'' + 1.163v''^2 \quad (7)$$

The value of u'' for which the spacings of the levels becomes zero is $u_0'' = 148$. By Eq. (5), $D_e'' = 25390$ cm$^{-1} = 3.13$ volts; by Eq. (6), $D_0'' = 3.11$ volts. The latter is the true heat of dissociation of the molecule $Ag^{107}Cl^{35}$. Its accuracy is estimated as ± 0.10 volt. This agrees closely with the value 3.1 volts taken from thermochemical data.*

For the excited state, extrapolation of the ω_u:u curve is somewhat uncertain. It is safe to assume however that a maximum value will be set by extrapolating a straight line drawn through the first three points. This gives $D_0' = 0.33$ volt. A lower limit may be set by calculating the area under the actual curve, using the empirical equation. This gives 0.28 volt. Hence we may take $D_0' = 0.31 \pm 0.02$ volt.

Theory of the Isotope Effect

The theory of the vibrational isotope effect, first formulated by Mulliken,[5a] has recently been applied in a form more convenient for calculation of isotope shifts in bands of high vibrational quantum numbers by Gibson,[6] Patkowski and Curtis,[7] and R. T. Birge.[4] Professor Birge has given a thorough discussion of the applicability of this method, and has kindly made his results available to the writer in advance of their publication. In the following, his notation will be followed, and some of his equations given. Superscripts i will refer to the "isotope" or less abundant molecule, while letters without superscript will denote the "main" or more abundant molecule.

The vibrational energy of a non-rotating molecule as given by Mulliken[5a] is $G_u = f(u\mu^{-1/2})$ where $\mu = M_1M_2/M_1 + M_2$, the effective or reduced mass of the molecule, M_1 and M_2 being the relative masses of the two atoms composing the molecule. If an isotope of one of the atoms is present, the reduced mass of the isotope molecule is μ^i, and if we let $\rho = (\mu/\mu^i)^{1/2}$ the vibrational energy of this molecule is $G_u{}^i = f(u\rho\mu^{-1/2})$. Hence for a given value of u, regardless of the functional form of G_u given by Eq. (1), we obtain $G_u{}^i$ by replacing u by $u\rho$. Writing Eq. (1) for the isotope molecule:

$$G_u{}^i = \omega_e[u\rho - x_e\rho^2u^2 + y_e\rho^3u^3 + \cdots]. \quad (8)$$

Subtracting Eq. (1) from Eq. (8) we obtain the general form of the isotope shift, as given by Birge:

$$G_u{}^i - G_u = \omega_e[(\rho - 1)u - (\rho^2 - 1)x_eu^2 + (\rho^3 - 1)y_eu^3 + \cdots]. \quad (9)$$

When an electron transition occurs, this becomes, in terms of the wave numbers of the origins of the bands,

* Taken from ref. 1.

[5a] R. S. Mulliken, Phys. Rev. **25,** 119 (1925).

[6] G. E. Gibson, Zeits. f. Physik **50,** 692 (1928).

[7] Patkowski and Curtis, Trans. Far. Soc. **25,** 725 (1929).

$$\nu_0^i - \nu_0 = \Delta\nu_0 = (\rho - 1)(\omega_e' u' - \omega_e'' u'') - (\rho^2 - 1)(\omega_e x_e' u'^2 - \omega_e'' x_e'' u''^2) + (\rho^3 - 1)(\omega_e' y_e' u'^3 - \omega_e'' y_e'' u''^3) + \cdots \quad (10)$$

Eq. (10) can be used for calculating the direction and magnitude of the isotope shift when the data are sufficient to give an analytic function representing the bands. This is more general than Loomis's Eq. (7)[8] and is in terms of half integral quantum numbers.

As shown by Birge, an approximate equation can be written for Eq. (9):

$$G_u^i - G_u = (\rho - 1)\omega_u u. \quad (11)$$

This gives, on transition,

$$\Delta\nu_0 = (\rho - 1)(\omega_u' u' - \omega_u'' u''). \quad (12)$$

The advantage of Eq. (12) is that it can be used independently of any functional form of G_u. It is necessary only to know the values of ω_u for the band whose isotope shift is to be calculated. The value of ω_u may be read directly from the ω_u:u curve, or interpolated linearly between $\omega_{u+1/2}$ and $\omega_{u-1/2}$, which are obtained directly from the spectrum.

This theory shows that the isotope effect is zero at the true origin of the band system. It also shows that the isotope shift does not increase uniformly as u increases. For, by differentiating Eq. (9) and equating the result to 0, a maximum value of the shift for a certain value $u = u_c$ is obtained. In case the ω_u:u curve is linear, u_c is approximately $1/2u_0$. The theory shows further that the apparent heats of dissociation D_e and D_e^i are equal. Geometrically, the ω_u:u curves for the main molecule and the isotope molecule cross each other at $u = u_c$, and the area under each is the same since $u_0/u_0^i = \rho$ and $\omega_e^i/\omega_e = \rho$. But the true heats of dissociation D_0 and D_0^i are not the same. The theory has been verified by Patkowski and Curtis[7] by application to the bands of ICl, and by Birge[4] to ICl and Cl_2, both of which involve isotope effects in the region of relatively high quantum numbers.

Isotope Effect in AgCl

The ω_u:u curves for the four isotopic molecules $Ag^{107}Cl^{35}$, $Ag^{109}Cl^{35}$, $Ag^{107}Cl^{37}$, and $Ag^{109}Cl^{37}$ are shown in Fig. 3. The curves for the excited states of the two Ag isotope molecules are not shown, since they almost coincide with the other two curves. The curves A'' and B'' for the normal states of the first set of Cl isotope molecules are very nearly parallel and show no intersection. But this is to be expected, since the extrapolated value of u_0'' was 148, and therefore u_c is about 74. However, the extrapolated values of ω_e for these molecules are in the ratio $336/343.6 = 0.978$, in close agreement with the calculated value of $\rho = 0.9794$. Also, for the strong pair of silver isotope bands, curves C'' and A'', the ratio $\omega_e^i/\omega_e = 342.4/343.6 = 0.997$ in close agreement with $\rho = 0.9977$. However, due to the slight uncertainty in determining the

[8] Bull. Natl. Res. Council, No. 57 (1926) p. 262.

TABLE III. *Isotope shifts.*

	$Ag^{107}Cl^{37}-Ag^{107}Cl^{35}$				$Ag^{109}Cl^{37}-Ag^{109}Cl^{35}$	
	$\rho-1=-0.020577$				$\rho-1=-0.020672$	
(v', v'')	$\Delta\nu$ obs	I $\Delta\nu$ calc	II $\Delta\nu$ calc	III $\Delta\nu$ calc	$\Delta\nu$ obs	$\Delta\nu$ calc
(2, 0)	—	−9.28	−8.27			
(3, 1)	−6.5	−6.42	−6.39	−8.08		
(4, 2)	−3.0	−2.72	−2.94	−5.77		
(1, 0)	−4.6	−4.56	−4.57	−4.81		
(2, 1)	—	−2.31	−2.30	−3.10		
(3, 2)	—	+0.45	+0.49	−1.12		
(0, 0)	—	+0.70	+0.69	+0.67		
(1, 1)	+2.5	+2.41	+2.39	+2.13		
(2, 2)	+3.5	+4.57	+4.58	+3.89		
(0, 1)	+7.2	+7.67	+7.67	+7.70		
(1, 2)	+8.6	+9.29	+9.24	+9.14		
(2, 3)	+9.5	11.35	11.37	10.77		
(3, 4)	12.8	13.93	13.92	12.67		
(0, 2)	14.3	15.84	14.54	14.68	14.4	14.56
(1, 3)	15.9	16.08	16.08	16.09	15.8	16.08
(2, 4)	17.7	18.04	18.06	17.69	18.0	18.03
(3, 5)	20.3	20.51	20.56	19.51	20.4	20.52
(4, 6)	23.4	23.86	23.63	21.63	23.3	23.86
(1, 4)	22.0	22.77	22.76	22.94	22.6	22.78
(2, 5)	24.2	24.63	24.65	24.51	24.1	24.65
(3, 6)	26.7	27.03	27.04	26.30	26.9	27.04
(4, 7)	29.6	30.25	31.94	28.36	30.3	30.29
(2, 6)	—	31.14	31.15	31.28		
(3, 7)	—	33.42	33.47	33.03		

TABLE III (*continued*)

	$Ag^{109}Cl^{35}-Ag^{107}Cl^{35}$		$Ag^{109}Cl^{37}-Ag^{107}Cl^{37}$	
	$\rho-1=-0.002264$		$\rho-1=-0.002360$	
(v', v'')	$\Delta\nu$ obs	$\Delta\nu$ calc	$\Delta\nu$ obs	$\Delta\nu$ calc
(1, 2)	—	—	—	1.04
(2, 3)	—	—	1.2	1.27
(3, 4)	—	—	—	1.55
(0, 2)	1.7	1.60	1.8	1.63
(1, 3)	1.9	1.77	1.8	1.81
(2, 4)	1.9	1.99	2.2	2.02
(3, 5)	2.3	2.26	2.4	2.29
(4, 6)	2.6	2.62	2.6	2.66
(1, 4)	2.5	2.50	3.0	2.56
(2, 5)	2.7	2.71	2.5	2.76
(3, 6)	3.0	2.97	3.1	3.03
(4, 7)	2.9	3.33	3.8	3.38
(2, 6)	3.3	3.43	—	3.49
(3, 7)	3.3	3.68	—	3.75
(4, 8)	3.8	3.95	—	4.09
(4, 9)	4.2	4.71	—	

proper slopes, it cannot be verified from the data that D_e is the same for all the molecules and D_0 different.

Curves A' and B' for the excited states of the first set of Cl isotope bands apparently show approach of intersection. The value of u_0' could not be accurately determined, but probably lies between 15 and 23. Hence the cross-over value u_c' is probably just outside the range of observation.

Table III contains the observed and calculated isotope shifts. Values of $\Delta\lambda$ were calculated from the mean of the observed displacements from the original measurements of the plates, and not the difference between the mean wave-lengths of Table I. The observed $\Delta\nu$ were calculated from these $\Delta\lambda$. The values of $\rho-1$ are also recorded in this table for the four sets of isotope bands. The main molecule in each case is written in italics. For the first set of Cl isotope bands, the calculated values of $\Delta\nu_0$ were obtained in three ways for comparison: column I using the approximate Eq. (12), column II the analytic Eq. (10), and column III the old equation $\Delta\nu=(\rho-1)\nu_u$ where ν_u is the difference between the wave-numbers of the head of the main molecule and ν_e, the origin of the band system. All three methods agree about equally well for most of the shifts. But Eqs. (10) and (12) are superior when high values of u' are involved. The old equation gives very poor agreement for bands having a high u' and low u''. This is to be expected, since III should agree asymptotically with I and II for low quantum numbers, and the greatest departure of III should occur when u is relatively high, as it is here in the excited state. The observed values of u in the normal state are relatively low.

The shifts for the other sets of isotope bands were calculated by Eq. (12). The observed shifts for the Ag isotopes are somewhat erratic due to the smallness of separation of the heads and their lack of sharpness, as well as their faintness in some cases. The results here confirm the existence of two isotopes of silver, of relative mass 107 and 109.

Products of Dissociation

It has been shown by Franck,[9] Dymond,[10] and others that when absorption of light by an "atom-molecule" results in dissociation by vibration from the excited state, at least one of the resulting atoms is excited. From a study of the ω_u:u curves in the normal state, Birge and Sponer[11] showed it quite probable that most molecules in dissociating by vibration from the normal state yield two normal atoms. The difference between the total energy (measured from the normal state) required to dissociate the molecule in the two cases should correspond to the amount of excitation of the resulting atoms. Hence, if a continuous spectrum exists which corresponds to the convergence limit of the $u''=0$ progression of the vibration bands, then by subtracting the lowest excitation energy in one of the resulting atoms from the long wave-length limit of this continuum, a value for the normal heat of dissociation D_0'' is obtained. For example, this was done by Dymond for I_2.

[9] J. Franck, Trans. Far. Soc. **22,** 536 (1925).
[10] Dymond, Zeits. f. Physik **34,** 553 (1925).
[11] Birge and Sponer, see ref. 5.

Conversely, if it is possible from the data for a given molecule to determine the heats of dissociation in both the normal and excited states, it is sometimes possible to find the states of the atoms resulting by dissociation.

In their work on the silver halides, Franck and Kuhn[1] report a continuous spectrum for AgI overlapping the discontinuous bands, and showing a maximum at λ3170. The long wave-length edge is variable with temperature and pressure. Assuming a normal silver atom and an excited (metastable) iodine atom formed by dissociation, and adding to this atomic energy the thermochemical value of D_0'', they obtained an energy value agreeing approximately with the observed long wave-length limit at λ3740. It appears to the writer that the use of the long wave-length limit of this continuum is in this case not at all reliable. Furthermore, the writer's conclusions as to the products of dissociation differ from Franck and Kuhn's. The use of the maximum at λ3170, which is on the high frequency side of the bands, would give close agreement. The same criticism would apply to AgBr. No continuous spectrum appeared with AgCl.

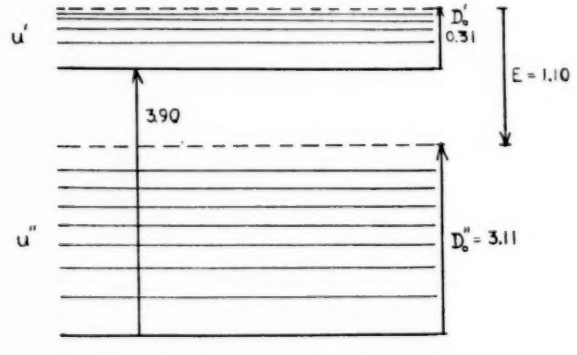


Fig. 4. Energy relations in AgCl.

Fig. 4 summarizes the results obtained in the present paper for AgCl. $D_0'' = 3.11 \pm 0.10$ volts, $D_0' = 0.31 \pm 0.02$ volt, and the energy corresponding to the (0, 0) band is 3.90 volts. This leaves 1.10 ± 0.12 volts as the electronic excitation of the atoms resulting by dissociation. In accounting for this energy, several possibilities must be examined. If the products are: (1) Ag^+ and Cl^-, the resultant energy would be the ionization potential of Ag minus the electron affinity of Cl, or $7.53 - 4.1 = 3.42$ volts. (2) Normal Ag and excited Cl; the separation $^2P_{1\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ in the normal state of Cl is 0.11 volt. This is the process which would be assumed consistent with Franck and Kuhn's conclusions. Other levels in the Cl atom may be excluded because of their high energy. (3) Excited Ag and normal Cl; this case was barred by Franck because of the large separation between the ^2P and ^2S levels of silver. (4) Both atoms excited.

The present results definitely exclude cases (1) and (2) even allowing a wide limit of error. However, (3) and (4) may be considered. Now in both Cu and Au there exist ^2D states between the ^2P and ^2S states, due to terms based

on the d^9s configuration of the ion.[12] The lines of the Ag spectrum have not been completely classified, but since Ag stands between Cu and Au in the periodic table, it is a plausible assumption that these low-lying states exist also in Ag.[13] If the silver halides dissociate into a normal halogen atom and a silver atom in this metastable $^2D(d^9s^2)$ state, then the electronic energy obtained as indicated in Fig. 4 should be *constant* for all three silver halides.

The writer has succeeded in assigning vibrational quantum numbers to Franck and Kuhn's data[1] for AgI and AgBr. This assignment is shown in

AgI

v'\v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	×	×	×	×	×	×	×	×		×	×	×	×	×
1	×	×	×			×	×	×						
2	×													
3	×													
4	×													

AgBr

v'\v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	×	×	×	×	×	×	×	×	×	×	×	×		
1			×		×	×	×	×	×					
2			×	×	×	×	×	×	×	×				
3														

Fig. 5. Assignment of vibrational quantum numbers to AgI and AgBr.

Fig. 5, which includes both absorption and fluorescence bands. Approximate equations representing the bands are as follows:

$$\text{AgI: } \nu = 31153 + 127.5v' - 5.7v'^2 - 205.7v'' + 0.57v''^2,$$
$$\text{AgBr: } \nu = 31421 + 179.4v' - 9.5v'^2 - 249.4v'' + 0.83v''^2.$$

This gives for AgI, $\omega_0'' = 205.7$ cm^{-1} and $\omega_0''x'' = 0.57$, and for AgBr $\omega_0'' = 249.4$, $\omega_0''x'' = 0.83$. These agree with the values deduced by Birge from Franck and Kuhn's data, 205.8, 0.56, 247.2, and 0.81 respectively.[14] On account of the uncertainty of the measurements, the $\omega_u : u$ curves are uncertain, and the heats of dissociation obtained by this data are not very accurate. But it is certain that the heats of dissociation in the excited states are very small and therefore a large error in determining them by extrapolation will not affect the results appreciably.

[12] Grotrian, Graphische Darstellung von Atomen . . . I, p. 73, II, p. 44, 51, A. G. Shenstone, Phys. Rev. **28,** 449 (1926) Cu.

[13] But the $d^{10}s$ configuration of Ag is expected to be more stable for Ag than for Cu or Au. See Hund's "Spectrallinien" p. 169–170; also R. Ruedy, Jour. de Phys. et le Radium **10,** 129 (1929); also Trans. Far. Soc. **25** (Dec. 1929) p. 752 (Bengtsson and Hulthén). For evidence of *instability* see J. Kaplan Zeits. f. Phys. **52,** 883 (1929).

[14] Int. Crit. Tables, Vol. V, p. 411 (Birge's table).

As in Fig. 4 we may now calculate approximately the resulting electron excitation E of the dissociation products by the sum $\nu_0+D_0'-D_0''=E$, where ν_0 represents the energy corresponding to the (0, 0) band. For AgBr and AgI we will use the thermochemical values[14] for D_0'' and the extrapolated values from the above analysis for D_0'.

$$\begin{aligned} \text{AgCl:}\ & 3.90+0.31-3.11=1.10 \\ \text{AgBr:}\ & 3.88+0.11-2.6\ =1.39 \\ \text{AgI:}\ & 3.85+0.09-2.0\ =1.94 \end{aligned}$$

The resulting values of E are thus not constant. But if we now subtract from these values of E the $^2P_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}}$ separation in the normal states of the halogens, which are respectively 0.11, 0.46, 0.94 volt[15] we obtain for E in the three cases 0.99, 0.93, 1.00 volt respectively, which is now very nearly constant. This indicates that the silver halides dissociate from the excited state into a silver atom in a $^2D(d^9s^2)$ state and a halogen atom in the $^2P_{\frac{1}{2}}$ state.

As in Cu and Au, combinations may occur in the silver atom between the ^2P and these $^2D'$ terms. Assuming the $^2D'$ level to be 0.99 ± 0.1 volt, or 8000 ± 800 cm^{-1}, above the normal ^2S level, we would expect a line in the Ag spectrum at 4400 ± 150A for the transition $^2P_{\frac{1}{2}}-{}^2D_{\frac{1}{2}}'$. There are several fairly strong unclassified lines in this region. Referring to Kayser's Handbuch Vol. VII, the two lines λ4888.3 (2u) and λ4677.9 (4u) have a wave-number separation 920 cm^{-1}, which agrees with the ^2P doublet separation. They are the only lines found giving this difference. Hence it is possible that they correspond to transitions $^2P_{\frac{1}{2}}-{}^2D'_{1\frac{1}{2}}$ and $^2P_{1\frac{1}{2}}-{}^2D'_{1\frac{1}{2}}$ in Ag. The next line of the same type as these two is λ4396.3 (2u). If this is the $^2P_{\frac{1}{2}}-{}^2D_{\frac{1}{2}}'$ line, this leaves 7731 cm^{-1} or 0.955 volt for the $^2D'-{}^2S$ separation. This is in close agreement with the above value $E=0.99$ volt deduced from the band spectrum of AgCl. Extrapolations such as were made in obtaining this value should be done cautiously. But even allowing a wide limit of error, the conclusions seem to be unaffected.

The above agreement may indeed be accidental, and awaits further testing by the final analysis of the Ag spectrum,* and by more accurate work on the band spectra of AgI and AgBr. The latter will be carried out by the author in the near future.

In conclusion, the writer expresses much appreciation for the valuable suggestions and constant interest of Dr. F. A. Jenkins, under whom this work was begun. I also am greatly indebted to Professor R. T. Birge for use of his manuscript on the vibrational isotope effect. Suggestions and interest of Dr. F. W. Loomis, and Dr. G. Breit were also helpful.

[15] L. A. Turner, Phys. Rev. **27**, 397 (1926).

* Dr. A. G. Shenstone has kindly informed me that his recent work on the Ag spectrum predicts these $^2D(d^9s^2)$ terms to be near 30000 cm^{-1}, close to the ^2P terms, with a doublet separation of about 5000 cm^{-1}. He believes that the lines mentioned above are due to the terms $^4P^\circ D^\circ F^\circ(d^9sp)$ combining with $^4D(d^9s, s)$, though he has not as yet been able to identify them. If this is correct, the value of E obtained by the writer remains unexplained.

THE RELATION BETWEEN THE INTENSITY AND POSITION OF THE OVERTONES OF SOME ORGANIC LIQUIDS

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Abstract

A theoretical study of the intensity relations of the overtones of some organic liquids has been made with a view of determining whether there exists a relation between the intensity and position of overtones. A brief summary of some of the work that has been done by other observers is included. By the graphical method the intensities of the first and second overtones of some liquids were measured. These results, together with the ratio of the intensities of the first and second overtones and also a list of the products of this ratio times the correction factor, x, are given in a table. Values are also listed for three diatomic gases, the intensities having been obtained by other observers and the ratio of these intensities times the correction factor being calculated in this work. For both the liquids and the gases the product of the ratio of the intensities of the first and second overtones and the correction factor, x, is of the same order of magnitude and, in consideration of the errors involved, appears to be constant.

A STUDY of the intensity relations of the overtones of some polyatomic molecules in the liquid state has been made with the purpose of determining whether there exists any relation between the relative intensities of the overtones and the correction factor as applied to the position of the bands. The position of an overtone is given by the relation, $\nu_n = n\nu_0(1-nx)$, where ν is the frequency of the overtone, n the number of the overtone, ν_0 the theoretical frequency of the fundamental band and x the correction factor. Some calculations have already been made on the intensity relations for the fine structure of gases by several observers. Dennison[1] has, through the aid of the correspondence principle, computed the intensities of certain infra-red bands in order to gain information concerning the structure of the molecule. He computed the intensities of harmonic bands of some diatomic molecules—HCl, HBr and HF. Since some of the constants used in the calculations depend upon a knowledge of the fine structure of the bands, the method could not be used generally. In order to check the results, the relative intensities of overtones were otained from experimental curves by taking for each band the maximum value of the absorption coefficient, α, rather than the actual value of the integral, $\int_0^\infty \alpha_\nu d\nu$.

The intensities of bands of symmetrical triatomic molecules and of axially symmetrical molecules with four atoms were studied by making certain assumptions concerning the relative positions of the atoms in the molecule, and it was found that the experimental and theoretical values were of the same order of magnitude.

[1] Dennison, Phil. Mag. **1**, 195 (1926).

Tolman[2] made some calculations of intensities of lines by graphical integration under the experimental curve for the absorption coefficient, and also by making the approximation of putting the integral, $\int_0^\infty \alpha_\nu d\nu$, proportional to the product of the maximum value of α_m and the spectral width, $\Delta\nu$, at which the value of α has sunk to one half its maximum value. This relation may be denoted by the following equation:

$$\int_0^\infty \alpha_\nu d\nu = K\alpha_m \Delta\nu.$$

Dennison,[3] in a more recent paper, has investigated the intensities and shapes of absorption lines of HCl. Formulae for comparing the relative intensities of a set of lines were developed. The area under the curve was measured in relative absorption times waves per cm.

The studies which have been briefly outlined above were all made upon the fine structure of the bands of gases. In the case of liquids this fine structure overlaps to such an extent that the individual lines cannot be observed at all, but only their envelope, which may be considered as the addition of all the separate lines in the band. In order to obtain the intensity of such a band the integral $\int_0^\infty \alpha_\nu d\nu$, was evaluated by the graphical method. The area under the curve was divided into a number of very narrow strips. The area of each strip was measured, and the sum of the areas of the rectangles taken as the area under the curve. The original curves were plotted in percent transmission as a function of spectrometer settings rather than in the coefficient of absorption as a function of waves per cm; however, the percent transmission was changed to coefficient of absorption by plotting a curve for each cell thickness showing relative transmission as a function of the coefficient of absorption. The relation between the relative transmission, I/I_0, the coefficient of absorption, α, and cell thickness, d, is given by the following equation: $\alpha = [\log (I/I_0)]/d$. In another curve the spectrometer settings were plotted against waves per cm. The dimensions of the small rectangles were found in terms of percent transmission and spectrometer settings. Each value was then changed to absorption coefficient or to waves per cm as the case might be. The curves which were used were greatly enlarged by projecting them on a piece of coordinate paper by means of a projection lantern.

Although a large number of measurements of infra-red bands have been made, most of them have been taken with prism spectroscopes of low resolving power and large slit width. The true shape of the band is lacking due to the width of the slit, and the true position of the band cannot be determined accurately due to the low resolving power of the instrument. The emphasis has been placed upon the position of the bands rather than upon their true shape. These and other inaccuracies make many curves which have been observed, useless for intensity calculations. However, in the work of Spence[4, 5]

[2] Tolman, Phys. Rev. **23,** 693 (1924).
[3] Dennison, Phys. Rev. **31,** 503 (1928).
[4] Easley, Fenner and Spence, Astrophys, J. **67,** 185 (1928).
[5] Spence and Easley, Phys. Rev. **34,** 730 (1929).

and his associates the absorption bands of several organic liquids have been measured with great accuracy. Their measurements were made with a grating spectrometer of slit width 0.25 mm. The settings were made with an accuracy corresponding to 0.5A. A grating with 10,000 lines to the inch was used up to 2μ. From this point on it was necessary to use a grating with 2,500 lines per inch. The entire range was gone over with cells of 1.4 cm, 0.7 cm, and 0.15 cm thickness. The absorption of the cell walls was compensated for by having two quartz plates of the same thickness of the cell walls to place in the beam of light when the cell was removed.

The relative intensity of the first and second harmonic bands of six different liquids as obtained by Spence and his associates was computed. Only six[4,5] were used since the remainder of the curves were very irregular. It was thought that some of these irregularities might have been due to overlapping of other bands.

If overtones exist for an harmonic oscillator, the ratio of frequencies of the successive harmonics to the fundamental should be 2:3:4, etc. Due to the anharmonic oscillation, strong overtones or harmonics occur in some substances, and their frequencies are found to be in the ratio $2\ \nu_0\ (1-2x)$: $3\ \nu_0\ (1-3x)$: $4\ \nu_0\ (1-4x)$, etc., where x is a correction factor. The correction factor, x, and the relative intensity of the harmonics are both functions of the anharmonicity of the oscillation, so it seems probable that there should be some definite relation between the two. That this is the case is shown by the present work. The results of the calculations are listed in Table I. There are

TABLE I. *The intensity of the first and second harmonics of certain liquids and gases and the ratio of these intensities times the correction factor, x.* (ρ_2^2 = intensity of first harmonic. ρ_3^2 = intensity of second harmonic.)

Substance	ρ_2^2	ρ_3^2	Thickness of cell	ρ_2^2/ρ_3^2	x	(Ratio) (x)
$CHCl_3$	352.62	97.50	1.4 cm	3.616	.0213	.082
$CHCl_3$	388.60	97.50	.7*	3.986	.0213	.085
$CHBr_3$	271.48	91.14	1.4	2.998	.0293	.088
$CHBr_3$	189.22	91.14	.7*	2.076	.0293	.061
$CH_2Cl \cdot CHCl_2$	363.40	84.48	1.4	4.302	.0174	.075
$CHBr_2CHBr_2$	377.32	195.88	1.4	1.926	.0391	.075
$CHBr_2CHBr_2$	376.70	195.88	.7*	1.923	.0391	.075
CCl_3CHCl_2	103.28	18.98	1.4	5.441	.0171	.093
$CHCl_2CHCl_2$	143.38	51.74	1.4	2.789	.0201	.056
CO				14.3	.006	.086
HCl				5.0	.017	.085
HBr				5.8	.013	.075

* 0.7 cm applies to the first harmonics only.

also listed in this table values for CO, HBr and HCl. The relative intensities of the overtones for these three substances were taken from the work of other observers[6,7]. The value for the relative intensity of the first and second overtones of CO is due to C. Schaefer and M. Thomas,[6] the value of x being given

[6] C. Schaefer and M. Thomas, Zeits. f. Physik **12,** 330 (1923).

[7] B. Burmeister, Verh. d. D. Phys. Ges. **40,** 589 (1913).

by Burmeister.[7] For HCl and HBr the values of x were computed from the work of Schaefer and Thomas. Using this and the value for the relative intensity of the fundamental and first overtone as given by Brinsmade and Kemble,[8] the relative intensity of the first and second overtones was computed by means of the equation for x as given by Dennison.[1]

Some very interesting relations can be noted in these results. In general as the value of x increases the ratio of the intensities of the first and second overtones decreases, or, in other words, as x increases the intensity of the harmonic band increases. The last column shows the product of the ratio and the value of x. It can be seen that this product is approximately a constant for the bands under consideration. The largest variation is in the value of $CHCl_2CHCl_2$. This discrepancy was not accounted for. The variation of the other values is well within the range of experimental error. The values for the three diatomic molecules, CO, HBr and HCl, as obtained by other observers are in excellent agreement with the results as obtained for the liquids.

In order to check the accuracy of the method used, the intensity of the first overtones of three different liquids was measured from the band obtained from a different cell thickness. The two values checked very closely except in the case of $CHBr_3$. There evidently was some error in the drawing of the curve for cell thickness of 0.7 cm. By reference to these curves[4] it can be seen that this band does not follow the form of the band for 1.4 cm cell thickness. For $CHCl_3$ the values checked very closely, and for $CHBr_2CHBr_2$ the check was almost perfect. The original bands did not extend to the 100 percent line, and some error was necessarily involved in the extrapolation of the bands to this line, but since the value of α is very small in this part of the band the error is not very great. In order to determine what possible error might be involved, one pair of curves was extrapolated in two ways, one extrapolation making the area much larger and the other making it much smaller than probable. It was found that the difference between the two areas amounted to about 10 percent.

While no general conclusion can be drawn from these results until a larger amount of data is available, yet it appears that, for the substances under consideration at least, the ratio of intensities of the first and second harmonic bands times the correction factor is approximately a constant.

The writer is indebted to Dr. E. K. Plyler who suggested the above problem.

[8] J. Brinsmade and E. C. Kemble, Proc. Nat. Acad. **3**, 420 (1917).

THE MAGNETIC SUSCEPTIBILITY OF RUBIDIUM

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Abstract

In view of the theoretical interest involved in Pauli's theory of paramagnetism, the author has reinvestigated the magnetic susceptibility of rubidium. The metal used is subjected to double distillation in vacuum to ensure purity. The technique employed for this is fully described. The susceptibility is determined at nine different field strengths ranging from approximately 9 to 25 kilogauss. No variation in the susceptibility of more than 2 percent is observed over this range. The estimated error in the mean value of the susceptibility is between 2 and 3 percent. The uniformity of the susceptibility, accordingly, shows absence of serious ferromagnetic impurity. The mean value of the mass susceptibility is found to be $+0.21_7\times10^{-6}$ at 20°C, the Pauli theoretical value being $+0.32\times10^{-6}$. A table is included showing the results found by all other investigators on this subject. The bearing of the results on the Pauli theory is discussed briefly.

I. Introduction

THE quantum statistics of an electron gas, first proposed by Fermi, has, in the hands of Sommerfeld, Pauli and many others, yielded much interesting information concerning the electrical and optical properties of metals. More particularly Pauli has applied these statistics to the calculation of the susceptibility of the alkali metals.[1] The agreement between theory and experiment in the case of the metals Na, K and Cs is, considering the nature of the Pauli calculation, quite remarkable.[2] In the case of rubidium however, upon which, up to the present work, three independent measurements have been made[3] very wide differences exist both between one another and the theoretical result. From the point of view of divergence from the theory rubidium appears to be distinctly "anomalous," and this is the more remarkable when it is seen that the allied element caesium is in good agreement with the theoretical value.

The author has accordingly made a new determination of the susceptibility of this element applying the methods used in his previous work on this subject. The results of this investigation are communicated in the following pages.

II. Preparation of the Metal

The rubidium metal was supplied by Messrs. Eimer and Amend, New York, and stated to be "chemically pure." Nevertheless it was felt that fur-

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[1] W. Pauli, Zeits. f. Physik **41,** 81 (1927).

[2] C. T. Lane and E. S. Bieler, Proc. Roy. Soc. Can. **22,** 117 (1928); C. T. Lane, Phil. Mag. **8,** 354 (1929).

[3] M. Owen, Ann. d. Physik **37,** 657 (1912); W. Sucksmith, Phil. Mag. **2,** 21 (1926); McLennan, Ruedy and Cohen, Proc. Roy. Soc. **A116,** 468 (1927).

ther purification would be desirable especially since it is highly important to avoid even minute traces of ferromagnetic substances. Accordingly the metal was subjected to double distillation in vacuum.

Figure 1 shows, schematically, the apparatus by which this was accomplished. The necessary high vacuum was produced by a Langmuir mercury pump, backed with a Cenco "Hy-vac" pump. The former had attached to it the usual liquid air trap (L) consisting of a bulb of nut charcoal.

The distilling apparatus proper consisted of bulbs B_1 and B_2 fitted with a charging tube F and a ground glass stopper W. The specimen tube, into which the distilled metal is received is shown at S. The latter consists of a thin walled glass tube, of uniform bore (about 0.4 mm) and some 18 cm long.

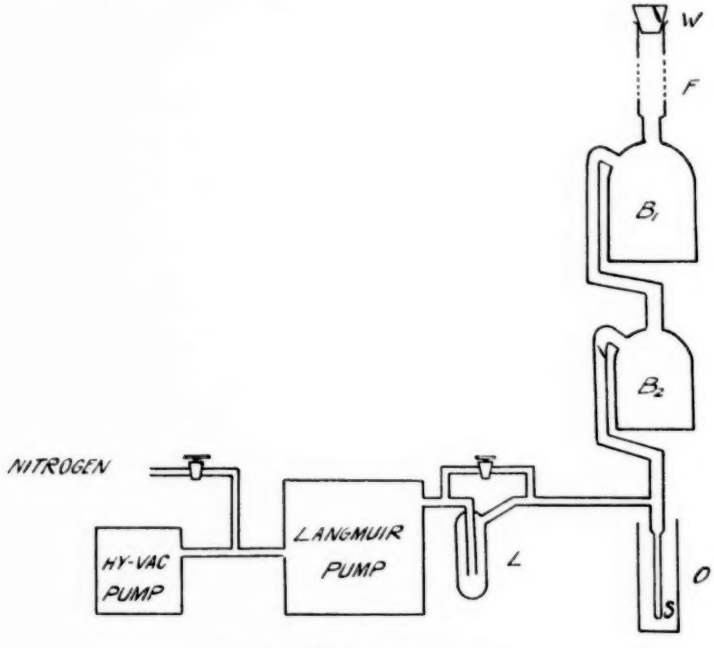

Fig. 1. Diagram of apparatus.

The diameter of the tube was uniform to within 1/5 percent. The whole apparatus was constructed of Pyrex glass.

The metal was received from the makers in 1 gr lots packed in a heavy oil. The tubes containing the metal were broken under petroleum ether, and the metal washed in two separate baths of the same material, and then quickly introduced into the charging tube F. While the charging was in progress a stream of nitrogen was kept flowing through the distilling apparatus. When the requisite amount of metal had been placed in F the nitrogen was cut off, the stopper W replaced and the whole apparatus pumped down. The metal was then melted into bulb B_1 and the tube F sealed off. An electric furnace was now paced over bulb B_1 and the metal gently distilled into bulb B_2. Bulb B_1 was then sealed off from B_2 and the operation repeated until about half the metal in B_2 was distilled into the specimen tube S. The latter was

kept in an oil bath at a temperature of about 70°C. This was allowed to cool down to room temperature, and then was sealed off from the main apparatus. The distillation process took about two hours to perform.

III. Method of Measurement

The Gouy method[4] for measuring the susceptibility was used wherein the specimen in the form of a long cylinder is suspended between the poles of an electromagnet, the axis of the former being perpendicular to the lines of force. The downward pull on the cylinder is given by the relation

$$P = \tfrac{1}{2} x A d (H_1^2 - H_0^2)$$

where P is the force in dynes; x the mass susceptibility; A the cross sectional area cylinder in cm^2; d the density of specimen in gr per cc; H_1 the field in gauss in the magnet gap; and H_0 the field in gauss at the other extremity of the cylinder. The pull P was measured with a balance accurate to 1/50 mg. The magnetic field was produced by a large Weiss electromagnet provided with water cooling arrangements. An aluminum housing was built around the magnet in order to shield the specimen from draughts. The former was provided with a celluloid front through which the specimen could be observed at all times. A thermometer could also be observed through this window. The water control allowed a very constant temperature to be maintained in the housing. The measurements were carried out at about 20°C.

Due to the fact that the glass tube containing the metal is diamagnetic a blank test had to be performed upon it, at the various field strengths used. After the measurement had been made on the metal, the tube was cleaned out and re-exhausted of air and the blank test made at the same temperature as the original measurement.[5]

The magnetic field was measured by means of a null method, developed by the author, which has been fully described previously.[6] A survey of the field in the vicinity of the magnet showed H_0^2 to be negligible compared to H_1^2.

IV. Results

The results of the measurement are given in Table I below, in each case the specific or mass susceptibility is quoted. In the first column is given the value of the exciting current in the magnet, in the second the force P corrected for the effect of the glass container and in the third and fourth the magnetic field intensity and mass susceptibility respectively. The density of rubidium (1.53) is the value quoted in "International Critical Tables."

The susceptibility is seen to be constant over the fie'd range used (approximately 19 kilogauss) to within about 2 percent which is within the experimental error.

[4] Stoner, "Magnetism and atomic structure," p. 40.

[5] This latter point is important since the susceptibility of glass varies greatly with temperature. Some rough tests on the glass used here (Pyrex) indicated that it had a temperature coefficient of approx. $\frac{1}{3}\%$ per degree C. The temperatures at which the two measurements were made agreed to within 1°C. See in this connection Gerlach and Little, Zeits. f. Physik **52,** 464 (1928).

[6] C. T. Lane, reference 2.

TABLE I. *Mass-susceptibility of rubidium (20°C).*

Current in Magnet Coils (Amps.)	Force (P) Milligrams	Magnetic Field gauss	Mass susceptibility
3.0	1.92	9400	$+0.21_8\times10^{-6}$
3.6	2.71	11160	0.21_6
4.2	3.75	13150	0.21_5
4.8	4.97	15020	0.22_0
5.5	6.30	17040	0.21_6
6.2	7.90	19060	0.21_6
7.0	9.47	20950	0.21_6
9.0	12.50	23830	0.21_9
12.0	14.24	25300	0.22_1

Mean value $+0.21_7\times10^{-6}$
Area cross section specimen $=0.1288$ cm^2
Density $=1.53$ gms per cc.

Owen[7] has shown that if iron be present in the specimen we should have the following relation between susceptibility and field strength, viz.

$$x = x_0 + \sigma/H$$

where x is the measured susceptibility; x_0 the "iron free" value of susceptibility; σ the saturation intensity of magnetization (per unit mass) of the uncombined iron impurity; and H the magnetic field intensity. The susceptibility should therefore decrease with increasing field according to an hyperbolic law if any noticeable ferromagnetic impurity be present. The susceptibility should be independent of field strength if no noticeable impurity exists, as is the case in the present experiment.

In Table II the various experimental results on rubidium are collected, together with the theoretically predicted value. The estimated accuracy of the present measurement is between 2 and 3 percent.

TABLE II. *Various results on mass-susceptibility of rubidium.*
(All values to be multiplied by 10^{-6})

Observer	Owen 18°C	Sucksmith 0°C	McLennan, Ruedy, Cohen	Author 20°C	Pauli (calculated)
Mass susceptibility	+0.07	+0.07	+0.17	$+0.21_7$	+0.32

V. DISCUSSION

It is seen that the result found by McLennan, Ruedy and Cohen is in close agreement with the present work. The divergence between these results and those of Owen and Sucksmith may perhaps be accounted for by the fact that in the latter experiments no especial precautions were taken to ensure purity in the specimens used.

The most remarkable feature is the wide difference between the experimental and calculated values, especially in view of the fact that the agreement between theory and experiment in the case of Na, Rb and Cs is remarkably

[7] M. Owen, reference 3.

close; nowhere differing by more than 10 percent of the calculated value. In this respect, then, rubidium seems to be anomalous.

We may recall that the Pauli formula for the susceptibility is

$$x = 12(\pi/3)^{2/3}\mu_0^2 n^{1/3} m_0 h^{-2} d^{-1} = 2.21 \times 10^{-14} n^{1/3}/d$$

where x is the mass susceptibility; n the number of free electrons per cc; d the density of the substance; μ_0 the value of the Bohr magneton; and m_0 and h have their usual significance. The only factor in this formula which might conceivably be incorrect is n, the number of free electrons per unit volume. Pauli makes the reasonable assumption that this is equal to the number of atoms per unit volume. Now in order to bring the theoretical value into agreement with the observed it would be necessary to suppose that n is actually about one-third its present accepted value, or rather, for some reason, only about one-third the number of free electrons per cc contribute to the paramagnetism. Of course we should not expect very close agreement with the Pauli formula since the latter neglects certain factors which should contribute to the susceptibility, viz.: (I) the diamagnetic effect of the atom cores; (II) a possible diamagnetic "induction" effect of the free electrons. We are at present unable to make any definite statement about the magnitude of these effects since no satisfactory theory for them has appeared.[8] All we can say is that the Pauli formula should produce higher values than those observed.

In any event the Pauli theory can only be considered as provisional since in its present form it is quite unable to account for at least two important observed facts, namely, the observations of McLennan, Ruedy and Cohen on the variation of susceptibility with orientation in single crystals of zinc and cadmium[9] and also on the observations of the author on the sudden change in susceptibility in passing over from the solid to the liquid state in the case of caes um.[10]

On the other hand, it must be remembered that it is the only theory in existence which even remotely gives the correct values for the susceptibility of the alkali metals, and further it accounts for that remarkable experimental fact that the susceptibility of the alkali metals (for a given state) is independent of the temperature.

In conclusion it gives me great pleasure to thank Dr. A. S. Eve, F. R. S. for his continued interest in this work. I am indebted also to Mr. H. G. I. Watson, Lecturer in Physics, for his aid in some of the numerical work.

[8] Cf. L. Rosenfeld, Naturwissenschaften **17,** 49 (1929). In this paper Rosenfeld has estimated the diamagnetic effect of the cores as a function of the "lattice potential" (V_0) of the metal. The quantity V_0 is estimated from G. P. Thomson and Rupp's data on electron beam diffraction experiments. Since only the order of the quantity V_0 is known the correction appears rather uncertain. In any event no data whatever exist for the alkali metals.

[9] McLennan, Ruedy and Cohen, Proc. Roy. Soc. **A121,** 9 (1928). In this paper the authors have apparently neglected to make a correction for the susceptibility of air which would have the effect of somewhat lowering their values. The values quoted for an isotropic crystal aggregate of Zn and Cd should be decreased by approximately 2.5 and 2.6 percent respectively. This brings their result into much better agreement with previous measurements.

[10] C. T. Lane, reference 2.

SECONDARY ELECTRONS FROM CONTAMINATED SURFACES

By Paul L. Copeland
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(Received February 21, 1930)

Abstract

Surface fields. —Small quantities of grease, or condensed vapors, or foreign metal upon a metallic surface have in the past been the cause of many spurious electrical effects. Stuhlmann and Compton cite a spurious contact potential difference of some 60 volts. Using electron reflection and secondary emission as a tool, some of the properties of such surfaces have been investigated. The results indicate that surface fields are set up retarding the reflected electrons.

Insulating layers. —New evidence is found for a sudden breakdown of the insulation of oils in thin films which has been investigated by Brüninghaus and by Watson and Menon. The bearing of the present results on suggested interpretations of the effect is briefly discussed.

THE fields in the neighborhood of incandescent filaments have been investigated[1,2] through a study of characteristics of the saturation curve. In the present investigation an attempt is made to study the fields in the neighborhood of cold metallic surfaces. The currents used are obtained by reflection and secondary emission of electrons at the surface to be studied.

Apparatus

The apparatus used is shown in Fig. 1. A filament, F, (of 7 mil tungsten wire) is placed at the center of a molybdenum cylinder, C, the diameter

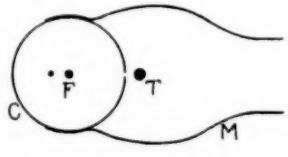

Fig. 1. Apparatus.

of which is about 1 cm. Electrons emitted by the filament are accelerated toward the cylinder by an applied potential. Some pass out through the slit (of width 0.25 mm) and strike the target, T, which is placed directly before it. The target consists of a second tungsten wire.

The potential of the cylinders, C and M, may be below that of the target, giving a field tending to prevent the escape of reflected electrons, or above it tending to accelerate them in their escape. With the cylinders at low potential, the escape may be almost entirely avoided; with C positive, the number

[1] Irving Langmuir, G. E. Rev. **23,** 503 (1920).
[2] Becker and Mueller, Phys. Rev. **31,** 431 (1928).

of electrons leaving may be greater than the primary ones which hit and the current to the target be actually positive.

The tungsten wire used for a target was in the earlier experiments a 10 mil and in the later experiments a 20 mil filament. This form of target was selected to facilitate the application of rather intense, homogeneous fields at its surface. With such a target, however, there is the danger that the full primary current will not strike it and, more serious, that the fraction which does strike it will vary as the field is changed. Fig. 2 shows the results of experiments performed to investigate this question. The current to the target was observed for different settings of the target near the slit as it was moved transverse to the slit. The numbered divisions correspond to motions of the target of approximately 1/7 cm or 0.056 in. transverse to the slit.

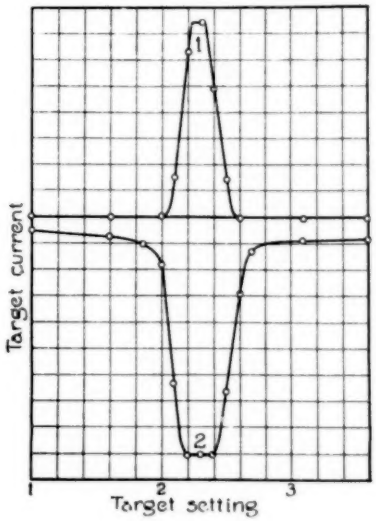

Fig. 2. Electron beam.

The curves in Fig. 2 show the results for a 20 mil target. The impacting speed was such as to produce large secondary emission in each case—in curve 1 this emission was allowed to leave; in curve 2 the field prevented secondary emission. In curve 1 the cylinders were maintained at a potential of 240 volts positive and the target 142 volts positive with respect to the source, *F*. Between the target and its surroundings was a potential difference of 98 volts, the field being in such a direction as to aid electrons in leaving the target. There is no current to the target until it comes into the direct electron beam from the slit. It rapidly approaches a maximum value and maintains this value while the target is moved about 1/7 mm transverse to the slit.

In the second curve, the target is 142 volts positive, but the cylinders have been lowered to 60 volts positive with respect to the source. The general shape of the curve is much the same as before except that the current is reversed in sense. The flat plateau on both of these curves indicates that the

target is larger than the electron beam and hence receives the full current for a number of settings. This result would be expected from the dimensions involved. When using a 20 mil filament, the target is enough larger than the beam so that the primary current can be considered constant as the field about the target is changed. Probably also a 10 mil target receives nearly all of the current through the slit.

Influence of the Surface Electric Field on Secondary Emission

To investigate the fields present at the surface of the target, the current carried by the target was observed as a function of the applied field, all the other conditions being held as nearly constant as possible. A given potential,[3] which for any single curve was held constant, was applied between the filament and the target. The effect of variation of secondary emission with bombarding velocity was thus eliminated. In the curves which follow, the abscissas give the potential of the cylinders, C and M, relative to the target. The ordinates give the net current to the target. Electron currents to the target are plotted as negative.

In the investigation of surface fields, a tungsten wire, without any special treatment whatever, was fastened in place as a target. The current to the target was then measured for different fields determined by the potential of the cylinders relative to the target, and the resulting curve was plotted. The target was then cleaned by heating it to incandescence,[4] and after this the observations of target current against cylinder potential were repeated. The difference in the shape of the two curves thus obtained indicates the influence of the impurities eliminated by the heating.

The curve indicated as number 1 in Fig. 3 was obtained soon after the target had been cleaned through heating it by an electric current. At the left of the curve, the negative current is not increasing; very few of the electrons are reflected with sufficient velocity to overcome these high retarding fields. As the potential of the cylinders is raised, an increasing number of electrons leave the target; this decreases the net current. The increase of the return current is particularly rapid when the retarding field is removed, for this enables the slow speed electrons to leave. Finally, the net current is reversed in sign; more electrons leave the target than strike it. In addition, then, to the electrons of the original beam which have been reflected, there must be others in the return current liberated by ionization at the surface. The positive current comes to a maximum value at once. This saturation of the secondary current with low positive potentials is exactly what we should expect; all the secondary electrons are able to leave the target if no field retards their escape.

The case is different, however, for targets which have surface contamination. The second curve indicated in Fig. 3 is one obtained just before the

[3] It was found that electrons of 100 volts energy produced secondary currents of suitable value, and in the curves which follow, the source was maintained 100 volts negative with respect to the target unless some other value is given.

[4] Such high temperatures were later found to be unnecessary for the removal of the impurities causing the pronounced effects observed.

heating of the target. The most significant feature is the poor saturation of the positive current. This must be due to retarding fields in the neighborhood of the target surface; otherwise we would expect all electrons emitted to be able to leave the target. This poor saturation appears to be the analogue of that observed for composite surfaces in thermionic emission. This has been explained as an effect of the fields in the neighborhood of the filament surface. Somewhat similar fields must exist here.

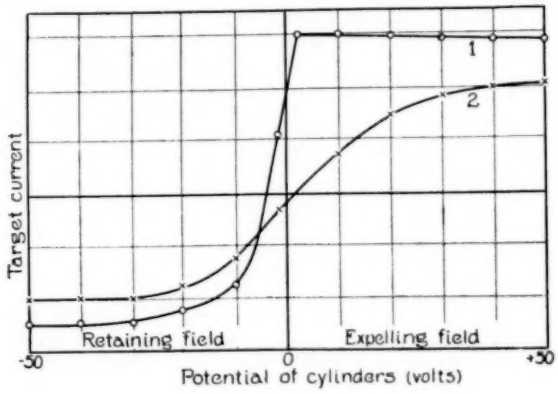

Fig. 3. Influence of electric field on secondary emission.

An attempt was made to observe by the present method fields due to thorium on a tungsten filament. That a surface field exists about an incandescent filament partly covered with thorium is known from saturation characteristics in thermionic emission. The results in the case of reflected electrons, however were not decisive. The effect of thorium on the saturation curve does not appear to be as pronounced as that due to the more easily volatilized impurities responsible for the above results.

Insulating Property of Thin Oil Films

The erratic behavior of metal surfaces contaminated by slight quantities of oil or wax have been at various times observed. Stuhlmann and Compton[5] in attempting to account for abnormally high velocities of photoelectrons showed that slight quantities of wax vapor could result in surface charges, sometimes as high as 60 volts, which acted in some respects as a contact difference of potential. A real contact potential difference of this amount is hardly plausible, and it would seem likely that the results are to be attributed to an insulating layer which was charged as high as sixty volts before the insulation broke down.

In the present experiment in the case of extreme contamination by oil particles, an interesting kind of "one way conduction" was observed which can be explained as due to an insulating layer. In the apparatus used for this experiment, the target was fastened onto wires entering the vacuum system

[5] Stuhlmann and Compton, Phys. Rev. **2**, 199 (1913).

through a stop-cock. Oil was placed around the top of the stop-cock; the stop-cock was then raised slightly from its socket, and the oil was injected into the system as a spray. The curve of Fig. 4, obtained after such treatment, follows the axis for a considerable range of potentials. The number of electrons striking the target in this range just equals the number leaving it. This rather striking result was confirmed by repeating the treatment several times.

To explain this we must suppose that the oil forms an insulating layer on the surface of the target which breaks down at some critical potential, apparently about 50 volts. The difficulty is that with retarding fields, even for small values of these fields, a negative current is indicated. To explain the entire curve on the basis of a continuous insulating layer would demand the assumption of some sort of one way conduction in the layer.

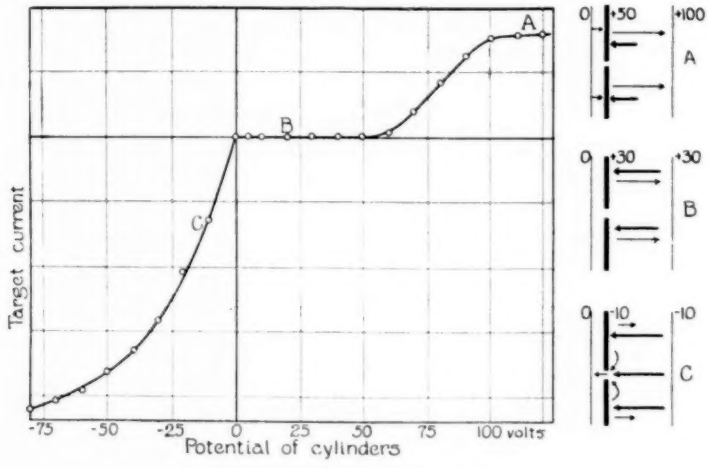

Fig. 4. Insulation due to oil film.

The curve can, however, be explained on two assumptions: first that the surface is only partially covered with minute droplets of oil, and second that these insulate only below some critical potential of about 50 volts; the insulation then breaks down. This leads to the insulation observed for small accelerating fields, which corresponds to the region *B* of the curve. The oil surface is raised by the more than one hundred percent reflection up to the potential of the cylinders,[6] and after this the secondary equals the primary current. The total current is zero. At higher potentials, such as in the region *A*, the insulation breaks down; electrons are supplied through the layer, and more than one hundred percent secondary current results. As soon as the potential of the cylinders has been reduced below that of the target, the primary and secondary currents find a way to the clean metal somewhat as

[6] See Fig. 3. The zero of current for the contaminated surface closely approaches the zero of the applied field. The zero of current does not usually fall more than five volts from the zero of applied potential. It should be noted that the argument used here does not depend upon the zero of current being exactly at the zero of the applied field.

shown in the lower sketch at the right of Fig. 4. This accounts for the negative currents indicated in the region *C*.

The apparent breakdown potential of this thin film is interesting. It has been known, of course, for some time that vaseline and other oils, which are ordinarily good insulators, may be used in thin films on electrical contacts to lower the resistance. The assumptions made above concerning this thin film and its breakdown potential appear to be in substantial agreement with the results of a number of rather detailed investigations[7,8] in which thin films (about 10μ thick) were included between two conducting planes to which a potential difference was applied. This was a simple and direct method of investigation; the results obtained could be interpreted quantitatively at once. The results obtained in the present experiment are of a more complicated nature; exact quantitative interpretations are perhaps impossible. The present verification of the effect, however, has some advantages. The results

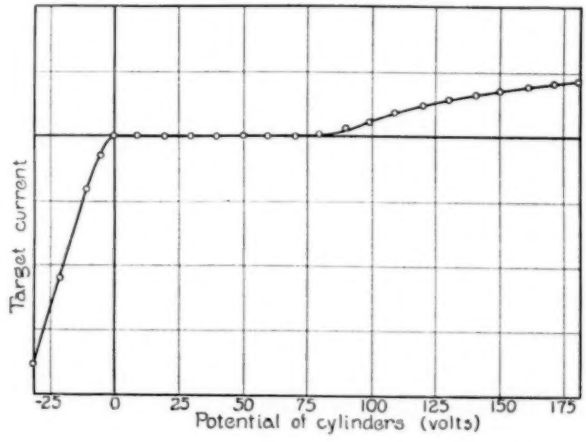

Fig. 5. Insulation at lower bombarding potentials.

of the present experiment eliminate the objection (possible in the case of the previous investigations although perhaps unfair in view of the care with which they were performed) that the breakdown obtained might be due to small projections of metal completing the circuit between the plates. In this experiment, small projecting areas are assumed to exist to explain the shape of the curves obtained. The breakdown, however, is evident; the positive current observed depends upon ionization over very considerable areas of the target surface to which the charge must be supplied through the oil. By the same argument, the experiment would seem to indicate something as to the nature of the phenomenon, because an explanation of the above results seems to demand the assumption of conductivity in the film over considerable areas. Some theories[9] have treated the conductivity as quite local.

[7] L. Brüninghaus, Comptes Rendus, **188,** 1386–88 (1929).
[8] H. E. Watson and A. S. Menon, Roy. Soc. Proc. **123,** 185–202 (1929).
[9] A. Gyemant, Phys. Zeits. **30,** 33–58 (1929).

It is probable, however, that the general electronic bombardment of the oil surface causes the disturbance to become quite general over the film. If, for instance, the theory of Güntherschulze[10] is correct and the breakdown is due to the movement of the ions in the film producing strong local heating with evaporation and the formation of gas bubbles in which the discharge takes place, it may be that the heating or the ionization produced by the impact of an electron would make such a breakdown more probable. The impact of electrons of the primary beam does in fact influence the breakdown. If the energy of the electrons striking the surface is greater than 100 volts, the breakdown occurs at a lower potential than indicated in Fig. 4. If the incident electrons are slow, the breakdown occurs at a higher potential. Fig. 5 shows the results for a bombarding velocity corresponding to 70 volts difference between the target and source. The curve follows the axis for a greater range of cylinder potentials than the curve of Fig. 4. The effect is even more pronounced at lower bombarding potentials.

In the present experiment, discharge does not occur between two metallic electrodes. The conduction appears to be from the metal to the surface of the film from which the charge may be dislodged only by electronic impact. The present results suggest that the conduction is continuous and general for the bombarded parts of the film.

Conclusions

The experiments reported here lead to the conclusions:

1. Strong fields are set up in the neighborhood of a contaminated surface retarding the escape of reflected electrons.

2. In extreme cases of oil contamination the impurities form an insulating film which breaks down at some critical value of the applied field.

3. The breakdown potential of a given film varies with the energy of the incident electrons.

4. The conductivity observed in these films appears to be rather general and continuous.

The writer wishes to thank the members of the staff of the Department of Physics of the State University of Iowa for their interest and assistance. Thanks are especially due to Professor J. A. Eldridge who suggested and directed the investigation.

[10] A. Güntherschulze, Jahrbuch d. Radioakt. u. Elektr. **19**, 92 (1922).

THOMSON EFFECT IN ZINC CRYSTALS

By L. A. Ware
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(Received March 4, 1930)

Abstract

The *Thomson coefficient*, σ, is directly determined for a group of zinc crystal rods with orientations distributed fairly uniformly over the entire possible range. At 49.5°C and at 125°C the values of σ seem to obey the Voigt-Thomson symmetry relation, although not as good a check is obtained at the higher temperature on account of increased experimental error. The principal values obtained are:

At 49.5°C, $\sigma_\perp = 0.98 \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$
$\sigma_\parallel = 0.38 \times 10^{-6}$ " " "
At 125°C, $\sigma_\perp = 2.09 \times 10^{-6}$ " " "
$\sigma_\parallel = 1.08 \times 10^{-6}$ " " "

The values at 49.5°C are found to compare favorably with values for polycrystalline zinc calculated from Sommerfeld's theory of conduction, (0.32×10^{-6} cal.·coul.$^{-1}$·deg.$^{-1}$), and found by Borelius experimentally, (0.88×10^{-6} cal.·coul.$^{-1}$·deg.$^{-1}$). The increase of σ with increased temperature is greater than has been previously reported for polycrystalline zinc but is in approximate agreement with some earlier determinations by the writer. In addition, *specific resistivity* and *temperature coefficient of resistivity* are determined.

Introduction

ABOUT two years ago the writer determined directly values of the Thomson coefficient for a few zinc single crystals[1] of orientations[2] near 0° and 90°. The main emphasis in this earlier work was placed on the variation of σ, the Thomson coefficient, with temperature, although it was possible to make some comparison with values of $(\sigma_\perp - \sigma_\parallel)$ computed from the previously published thermal e.m.f. determinations of Linder,[3] Bridgman,[4] and Grüneisen and Goens.[5] Following the work just mentioned, some determinations of σ were made at a single temperature, (about 50°C), on a group of crystals covering a wider range of orientations, particularly with a view to checking the Voigt-Thomson symmetry relation for the Thomson coefficient. These crystals were a by-product of the investigations of Tyndall[6] and of Hoyem and Tyndall[7] and were therefore grown under somewhat different conditions and

[1] M. S. Thesis. University of Iowa, 1927; not published.

[2] Orientation, for a hexagonal crystal, is defined as the angle between the main crystallographic axis and the length of the specimen.

[3] E. G. Linder, Phys. Rev. **26,** 486 (1925); **29,** 554 (1927).

[4] P. W. Bridgman, Nat. Acad. Sci. Proc. **11,** 608 (1925); Proc. Amer. Acad. Sci. **61,** 101 (1926).

[5] Grüneisen and Goens, Zeits. f. Physik **37,** 378 (1926).

[6] E. P. T. Tyndall, Phys. Rev. **31,** 313 (1928).

[7] A. G. Hoyem, and E. P. T. Tyndall, Phys. Rev. **33,** 81 (1929).

throughout a rather long period of time. It is certain also that the zinc came from several lots (although of the same kind of zinc). In view of other work done recently in this laboratory, it is not now surprising that such a miscellaneous series of crystals failed to give very consistent results. In particular σ was not determined as a definite function of the orientation. A third series covering a good range of orientations was therefore prepared by Mr. Hoyem. The crystals were made consecutively, were grown at the same rate, were of very nearly the same diameter, and the zinc came from only one original container. The material was Kahlbanm's best zinc. The work reported herein consists mainly of a direct determination of the Thomson coefficient at two temperatures (49.5°C and 125°C) for each crystal of this last series. From these data it is possible to check the usual thermodynamic theory of thermoelectricity and to test the Voigt-Thomson symmetry relation directly for σ.

In addition the specific resistance at 20°C and the temperature coefficient of resistivity were measured, mainly as tests for purity of the zinc, freedom of the crystals from strain, etc.

Apparatus and Experimental Procedure

The Thomson coefficient was measured in the fashion described by Nettleton[8] with some slight modifications which are described below. In this method the two ends of the specimen, which is a short wire or rod, are kept at constant, but different temperatures. At the same time a current, I_1, is passed in such a direction through the specimen that the Thomson effect causes a generation of heat. If this current is reversed the temperature at the center of the specimen will decrease slightly, as the Thomson heat is now being subtracted. If, however, on reversal, a suitable increase in the current, to I_2, is made an extra generation of Joulean heat compensates for the previous loss and the temperature remains unchanged. The apparatus is designed to measure directly the difference between I_2 and $I_1(=i_0)$ and to detect, with a bolometer coil and a Wheatstone bridge, any change in temperature at the center of the crystal, so that the state of zero-change may be found. Let R represent the resistance of the crystals, U, the difference in temperature between the two ends, and J, the constant 4.18 joules per calorie. Then, as Nettleton has shown, the Thomson coefficient, σ, will be given by the equation, $\sigma = i_0 R/JU$ cal.$\cdot$coul.$^{-1}\cdot$deg.$^{-1}$ provided certain conditions are satisfied. It is believed that all these are satisfied in the present work except that the crystals were made longer than Nettleton considered because of their very low resistance. The heat insulation was improved greatly, however, over previous methods and it seems certain that the equation is satisfactory for the lengths and diameters used.

To determine the specific resistance, ρ, and the temperature coefficient of resistivity, α, curves were plotted for resistance against temperature between room temperature and 110°C. For a linear relationship between resistance and temperature, α is given by;—

[8] H. R. Nettleton, Proc. Phys. Soc. Lond. **34,** 77 (1921); **29,** 59 (1916).

$$\frac{1-p}{t_2p-t_1}$$

in which $p=R_1/R_2$; R_1 and R_2 being resistances measured at temperatures t_1 and t_2 respectively. The specific resistance at any temperature is given by:

$$\rho = RM/\delta L^2$$

where R is the resistance at the desired temperature, M is the mass of the crystal, δ is the density, and L is the length. The resistance measurements were made by the usual potentiometer method, the crystal being immersed in a constant temperature oil-bath heated by an electric heating coil. The bath could be adjusted easily for any temperature between room temperature and 125°C. In this case, room temperature to 110°C was used as the range.

Fig. 1 shows the arrangement of apparatus used to measure the Thomson coefficient. The details of the terminals H and C will be considered with Fig. 3. In Fig. 1, H represents the hot end of the crystal and C, the cold. V is

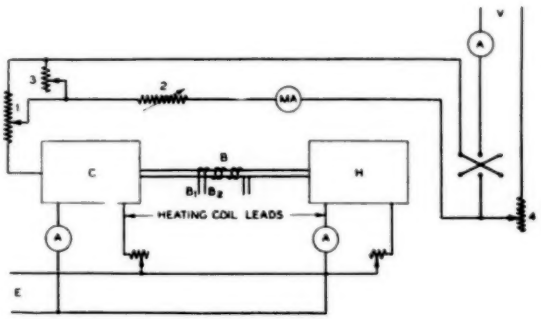

Fig. 1. Apparatus wiring diagram.

a source of 12 volts for which storage batteries were used so that the current would be as uniform as possible. B_1 and B_2 represent the two bolometer coils wound around the middle third of the crystal for the purpose of detecting a change in temperature when the current through the crystal is reversed. Apparently only one coil was used by Nettleton, but the use of two coils in opposite arms of the Wheatstone bridge was adopted on account of the increased sensitivity. The bridge is shown in Fig. 2. Actually the windings of B_1 and B_2 are interspaced as shown in Fig. 1 although shown separated in Fig. 2 to render the electrical connections clearer. In Fig. 1 the resistance 1 is about 10 ohms, 2 is a 500 ohm resistance box adjustable to 0.1 ohm, 3 is a rheostat of 2000 ohms, and 4, which controls the main current, is 47 ohms. The switch S is especially constructed to be very rapid and of very low resistance. E is a source of 110 volts A.C. supplying the heater coils at both ends of the crystal.

Fig. 3 presents the method of producing the constant temperatures at the ends of the crystals. Brass blocks were turned down to make the pieces A and

B, each about one inch in diameter and 1.5 inches long. A was threaded into the end of the basin C so that the crystal could be directly connected to it. An opening D was made in A to facilitate the circulation of water. On A, a heating coil was wound of No. 24 Karma wire and leads taken out. The heating coil was used to melt the solder for the purpose of either putting the crystal in place or removing it. A screen partition, E, was placed as shown to prevent the ice getting into the stirrer. This arrangement maintained the cold end of the crystal very constantly at about one degree above 0°C. At H, a double

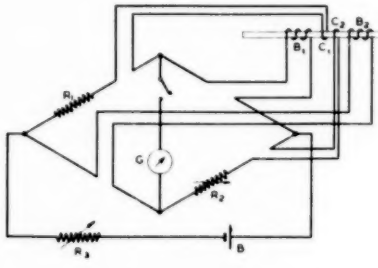

Fig. 2. Wheatstone bridge connection.

cylinder was used with heat insulating powder in the space F. The block, B, was similar in all respects to A, it being threaded into the end of the cylinder, and having a heating coil for the double purpose of mounting the crystal and heating the enclosure to a constant temperature when readings were being made. During an experiment the space, G, was filled with water and maintained by the heater at very nearly the boiling point. The thermometer, T, was used to read the temperature. By keeping the current about 0.9 ampere, B could be maintained at a remarkably uniform temperature for about three hours. Thus was obtained a very satisfactory method of maintaining a tem-

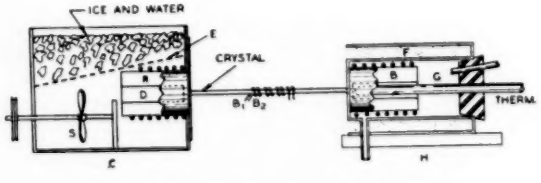

Fig. 3. Details of hot and cold terminals.

perature difference of about 97°C for a considerable length of time and it proved to be a much better method than that used later in obtaining the results for an average temperature of 125°C.

The details of the bridge circuit are shown in Fig. 2. Here, R_1 is a fixed resistance of about 6 ohms which, with as much of the wiring as possible,was inclosed in a heat insulated box. R_2 is a resistance made up of shunts across a coil, similar to R_1, and in series with a slide wire resistance of 0.1 ohm capable of adjustment to about 0.01 ohm. The function of the two coils, B_1 and B_2, has

been described already. The compensating coils, C_1 and C_2, are used to decrease the drift of the galvanometer due to the change of resistance of the leads to B_1 and B_2. B_1, B_2, and R_2 as well as R_1 are all about 6 ohms resistance. The bolometer coils and compensators were constructed of No. 40 copper wire silk insulated. The Wheatstone bridge thus arranged proved to be much more sensitive than the arrangement used in the previous work, which contained only one bolometer coil and no compensating coils.

For the purpose of determining σ at the average temperature of 125°C it was necessary to make a few minor changes in the arrangement shown in Figs. 1 and 3. In Fig. 1 the source, V, was reversed as well as all the meters contained in the circuit. A little inspection will demonstrate that this allows the measurement of positive σ* if H and C are also interchanged. In this case the method of heating H was unchanged, it being, as before, maintained near the boiling point of water. However, the ice water in C was removed and polarine oil was substituted. The heating coil on A was brought into use and the temperature of the oil maintained at about 150°C. Here it was rather difficult to maintain the temperature sufficiently constant, a condition which slowed the procedure somewhat. The temperature at the hot end of the crystal was measured by a sensitive thermometer placed in the opening, D. The readings of the thermometers at both ends of the crystal were checked by means of thermocouples connected to the face of A and B near the ends of the crystal. It was found that the temperature gradient determined from the readings of the thermometers differed from the actual gradient by about 2 percent. In computing the results, a suitable correction was, of course, made.

Measurements on the crystals were taken as follows. First a crystal is carefully cut to about 9 cm length, weighed, and to each end is soldered, by a very small amount of solder, a small copper wire, at about the middle of the wire, so that its two ends can serve as current and potential leads, respectively, for the resistance measurements. The crystal is then suspended in the oil bath, the heater in the oil bath is adjusted for the desired temperature, and the assembly is allowed to stand until the temperature, as indicated on a calibrated thermometer, is steady. A current of 0.3 ampere is then sent through the crystal and the P.D. read on the potentiometer. The current is reversed and readings made again. The average of four readings, (two in each direction), gives sufficient data to determine the resistance at this particular temperature. This is repeated for six or seven different temperatures and a curve plotted from which ρ and α can be determined.

After these data have been obtained the crystal is taken from the oil bath, the leads unsoldered, and two bolometer coils wound on at the center as indicated above. The heaters A and B of Fig. 3 are then started and when sufficiently hot the crystal is soldered closely against the face of A and B as there indicated. It is necessary in this procedure to be very careful not to strain the crystal. When the crystal has been fastened in place and the bolometer and compensating coils have been connected to the bridge, kieselguhr is

* σ is positive if heat is generated for current flow down the temperature gradient.

packed into the space between A and B and around the crystal to a radius of about 5 cm. Over this is packed a considerable amount of cotton and the apparatus is ready for the establishment of a temperature gradient. The space, G, is filled with water, and with the thermometer in place the current is established through the heater, B. It is given a high value at first and as the temperature approaches 98° or 99°C it is reduced to 0.9 ampere, where it is left. In the meantime, with the current shut off in A, the container is filled with water, the screen put in place, and the space above the screen filled with cracked ice. The stirrer is then started and the whole assembly is allowed to attain a steady state. As it begins to approach such a state the currents through the Wheatstone bridge and through the crystal are established. A determination of the balancing current, i_0, is made as follows: Referring to Fig. 1, it is seen that with the switch, S, to the left the main current divides, part going through the crystal and part through the milliammeter, M.A. When S is thrown to the right all the line current goes through the crystal. Thus the current through the crystal has been increased on reversal and if the rheostats 1 and 3 are correctly adjusted, the milliammeter, for any particular setting of resistance 2 and the main current, will read the same for either position of the switch, S. In this case the reading of the milliammeter is the i_0 required in the working equation. Thus it is necessary first to adjust resistances, 1 and 3, (Fig. 1), so that the milliammeter reads the same for both positions of S, then, if the system is otherwise balanced, some value of i is tried and the bridge, (Fig. 2), is adjusted for left position of S. Switch S is then thrown to the right and if the bridge indicates a decrease of temperature at the center of the crystal, i is increased, and the procedure repeated until it is just determinable that the current, i, is too low. A similar process is gone through with i being successively reduced from a value initially too high. The balancing current, i_0, is the mean of these two limiting values of i. The difference between these two values is generally less than 10 percent of i_0.

The procedure for the determination of σ at the higher temperature, 125°C, is similar to that at 49.5°C. However, in this case it should be pointed out that it was not so easy to maintain a constant temperature at the hot end. This introduced a certain amount of unsteadiness, and a corresponding decrease in the reliability of the results.

Results

The experimental results are exhibited graphically in Figs. 4 and 5. The specific resistance will be considered first. It is plotted in Fig. 4 against the square of the cosine of the orientation. This plot should yield a straight line since the validity of the Voigt-Thomson law for specific resistance of zinc crystals has been established, particularly by Bridgman.* The solid straight line shown is that for data recently obtained by Bridgman.[9] It is actually drawn by him through the lowest of his points, in spite of the fact that the

* The Voigt-Thomson symmetry relation states that the thermo-electric effects in crystals plotted against the square of the cosine of the angle of orientation should yield a straight line.

[9] P. W. Bridgman, Proc. Am. Acad. Arts and Sc. **63,** 351 (1929).

scattering of his observations is about half as great as that shown in Fig. 4. This procedure is justified by his discovery that any very slight strain raises the resistance of a zinc crystal. Five of the writer's crystals were therefore rechecked with the purpose of determining what effect resulted from intentional slight strains. The points so obtained are indicated by triangles. In two cases the resistivity changed and it increased. Of the three crystals which

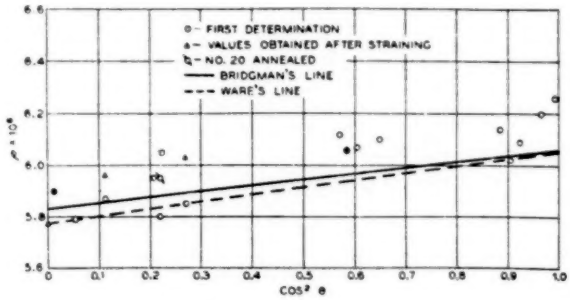

Fig. 4. Specific resistivity in ohms per cm³ plotted against $\cos^2\theta$.

did not change in resistivity, two already had high values and the other probably was not very much strained as it was a 90° crystal and therefore stiff. The greatest increase was about 3 percent. It will be noted also that the value for crystal No. 20, ($\rho = 5.8 \times 10^{-6}$, $\cos^2\theta = 0.22$) has increased due to annealing. However, this crystal has shown very inconsistent results in other respects. Following the idea of Bridgman that the lowest values are more probably correct, the dashed straight line has been drawn through four low

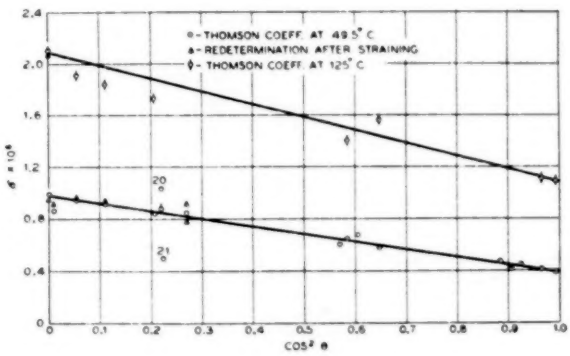

Fig. 5. The Thomson coefficient in cal.·coul.$^{-1}$·deg.$^{-1}$ as a function of $\cos^2\theta$.

points neglecting the point for crystal No. 20. The values of ρ obtained from this line for $\cos^2\theta = 0$ and $\cos^2\theta = 1$ are: $\rho_\perp = 5.78 \times 10^{-6}$, $\rho_\parallel = 6.05 \times 10^{-6}$. These given for $(\rho_\parallel - \rho_\perp)$, **0.27** whereas Bridgman obtains **0.23**. Bridgman's ratio $\rho_\parallel/\rho_\perp$ is **1.04** while the values above yield **1.05**. Grüneisen and Goens obtain **1.08**. The agreement with Bridgman in the matter of specific resistance and the effect of strains is quite satisfactory.

The variation of resistance with temperature, between 20°C and 110°C is for all but four of the crystals accurately linear. These four show only a very slight deviation. The temperature coefficient, α, was therefore computed in the manner explained above. The values of α lie between 0.00413 and 0.00437 and show no very certain variation with orientation. The average value is **0.00425**, a value about 2 percent higher than that obtained by Bridgman.

The values of the Thomson coefficient for both 49.5°C and 125°C are presented in Fig. 5. If the best straight line is drawn through the points for 49.5°C it will be found that the deviation from the line is, in all except two cases, within the experimental error. These two cases are those of crystals No. 20 and No. 21, ($\theta = 62°$). No. 20 has already been mentioned in the case of resistivity as being anomalous and here it is seen that even at 125°C the value of σ is lower than for 49.5°C. Also, No. 20 was annealed, as mentioned before, and the same value for σ was again obtained at 49.5°C. There was no visible evidence of No. 20 or No. 21 being different from the other crystals and the explanation of their deviation is not readily apparent.

Although a straight line has been drawn through the points for 125°C, the writer does not claim that the data afford a test of the Voigt-Thomson symmetry relation at this temperature. The deviations from the line as drawn are no greater, however, than the experimental error at this temperature. Moreover the value of $(\sigma_\perp - \sigma_\parallel)$, obtained from this line and stated just below agrees as well with indirectly determined values as is the case at 49.5°C.

The values of $\sigma_\perp$ and $\sigma_\parallel$ at 49.5°C are $\mathbf{0.98} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ and $\mathbf{0.38} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ respectively. Thus a value of $(\sigma_\perp - \sigma_\parallel)$, $\mathbf{0.60} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ results. From the relation, $(\sigma_\perp - \sigma_\parallel) = T\, d^2E/dT^2$, Bridgman[9] obtains $\mathbf{0.661} \times 10^{-6}$, Grüneisen and Goens,[5] $\mathbf{0.622} \times 10^{-6}$, and Linder,[3] $\mathbf{0.521} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ At 125°C the writer obtains the value $\mathbf{1.01} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ as compared with Bridgman's[9] $\mathbf{0.813} \times 10^{-6}$, Grüneisen and Goens' $\mathbf{1.12} \times 10^{-6}$, and Linder's $\mathbf{0.795} \times 10^{-6}$ cal.·coul^{-1}·deg.$^{-1}$ Borelius and Gunneson[10] have made measurements on several polycrystalline metals and obtain for zinc at 49.5°C, $\mathbf{0.885} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ Taking $\sigma_{54.5}$ as representative of σ in polycrystalline zinc, the writer obtains $\mathbf{0.78} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ The difference in purity of the material used by the various investigators may well account for the rather wide range of values obtained.

In general it can be said that the observation of Bridgman concerning resistivity is substantiated. The average value of α obtained is slightly higher than that given by Bridgman and there appears to be a somewhat greater difference between $\alpha_\perp$ and $\alpha_\parallel$ than that which Bridgman finds. The values of $(\sigma_\perp - \sigma_\parallel)$ for 49.5°C agree with those calculated by the thermodynamic formula from the previously observed thermal e.m.f. vs. temperature curve. The Voigt-Thomson relation is supported within the limits of error by the data on $\sigma_{49.5}$. The data on $\sigma_{1.5}$ are presented for what they may be worth.

Sommerfeld,[11] by an extension of his theory of electrical conduction, has

[10] G. Borelius and F. Gunneson, Ann. d. Physik **65**, 520 (1921).

[11] A. Sommerfeld, Zeits. f. Physik **47**, 143 (1928).

developed an equation for the Thomson coefficient which to the first approximation is:

$$\sigma = \frac{2\pi^2}{3} \frac{mk^2T}{eh^2} \left[\frac{8\pi}{3n}\right]^{2/3}$$

which is seen to be dependent on T, the absolute temperature, and n, the number of atoms per cc, only as variables. This, calculated for zinc, gives, at 49.5°C, 0.32×10^{-6} cal. · coul.$^{-1}$ · deg.$^{-1}$, a value agreeing, in order of magnitude with existing data.

No theory has been developed for the Thomson effect in single crystals, although Houston[12] has extended his work in this direction.

The writer wishes to express his thanks to Dr. E. P. T. Tyndall, under whose direction this work was undertaken, for his help and encouragement at all times. He wishes also to thank Mr. Hoyem for so kindly consenting to grow the crystals used in this work. Thanks are also extended to members of the department for their advice and suggestions.

[12] W. V. Houston, Zeits. f. Physik **48**, 449 (1928)

E.M.F., RESISTANCE, AND CAPACITANCE PHENOMENA IN PHOTOVOLTAIC CELLS CONTAINING GRIGNARD REAGENTS

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Abstract

E.m.f., resistance, and polarization capacitance have been measured in light-sensitive cells containing ether solutions of Grignard reagents in an effort to determine whether the known voltage variations with illumination are due to ionization changes or to electrode-film variations. Voltage alterations with illumination or x-ray irradiation are described. Resistance variations with illumination are found in ethylmagnesium bromide cells but not in phenylmagnesium bromide cells until a "forming" process has been carried out. Solvation changes seem to offer a more reasonable explanation than ionization changes. Capacitance changes seem unrelated to resistance or voltage changes. Unsymmetrical resistances are noted in several cases. Capacitances as high as 7 mf per cm² of electrode area have been found. Film thicknesses are estimated to be of approximately molecular dimensions, greater for benzene-ring compounds than for short-chain compounds. Voltage variations are thought to be due to phenomena taking place on or very near electrode surfaces.

THE Becquerel effect is the name applied to an alteration of the electromotive force of a voltaic cell upon exposure of the cell to light. Originally found by Becquerel[1] to take place in a cell having platinum or silver plates coated with a silver halide and immersed in dilute sulphuric acid, the effect was later discovered by Rigollot[2] to exist with solutions of fluorescent dyes. Now the effect is known to be very common. Through the work of Nichols and Merritt,[3] Hodge,[4] and others, the effect has been shown to be located at or very near the electrode surface in the case of the dye solutions. Goldmann[5] offered a theory based on the photoelectric effect. Baur[6] proposed a photochemical theory for the effect, which has been upheld by Garrison,[7] Tucker,[8] and Russell[9] among others. A reasonably comprehensive survey of the work carried on with solutions in water and in absolute alcohol is presented by Lifschitz and Hooghoudt.[10]

[1] E. Becquerel, Compt. Rend. **9,** 145 (1839).
[2] M. H. Rigollot, Compt. Rend. **116,** 878 (1893).
[3] Nichols and Merritt, Phys. Rev. **19,** 415 (1904).
[4] P. Hodge, Phys. Rev. **28,** 25 (1909).
[5] A. Goldmann, Ann. d. Physik **27,** 449 (1908).
[6] E. Baur, Zeits. f. Phys. Chemie **63,** 683 (1908).
[7] A. D. Garrison, Jour. Phys. Chem. **28,** 334 (1924).
[8] C. W. Tucker, Jour. Phys. Chem. **31,** 1357 (1927).
[9] H. W. Russell, Phys. Rev. **32,** 667 (1928).
[10] Lifschitz and Hooghoudt, Zeits. f. Phys. Chemie **128,** 87 (1927).

A number of papers have been published on the luminescence of Grignard compounds, organo-magnesium halides, under suitable conditions.[11,12] Kondyrew[12] showed that cells containing ether solutions of ethylmagnesium bromide produced an e.m.f. He also measured the temperature-resistance coefficient. Such cells show the Becquerel effect.[11,12] Considerable work, much of it as yet unpublished, has been done by others on the variation of the e.m.f. of Grignard cells with changes in illumination, in wave-length of light used, in temperature, etc.

The primary purpose of this investigation was to uncover new evidence as to whether the photovoltaic effect in Grignard cells took place on or near the electrodes or in the body of the electrolyte. A photoelectric effect should produce a change in the conductivity of the solution and an alteration in an electrode film might cause a detectable change in the cell capacitance. The method employed contemplated tests of many such cells, first as to the nature and magnitude of e.m.f. alterations, second as to the existence and magnitude of any resistance and capacitance changes under exposure to light or to x-rays. The results obtained suggested a further investigation of certain of the effects of electrolysis on these cells, a feature not originally planned. Certain interesting results were obtained.

Most of the cells were made up in one-inch test tubes with the electrodes mounted on glass tubes passing through rubber stoppers. The supporting wires were either of the same materials as the electrodes or else the electrodes were long enough to keep the wires out of the solutions. A few H-cells with one electrode in each arm were used. Some cells hermetically sealed in glass were made, since it was desired to test whether the properties were retained for a long time, if the evaporation of the ether was prevented. The Grignard reagents were made in an atmosphere of nitrogen, but in the solution there may be formed an etherate of the magnesium halide. It has not been possible to determine how far these etherates influenced the actions noted. The compounds used were phenylmagnesium bromide, ethylmagnesium bromide, the corresponding iodides, and bromo-ethylmagnesium bromide. These compounds were used because previous work by others had shown that they gave the largest photovoltaic responses. Various concentrations and electrode combinations were used.

The cells were mounted in a constant-temperature water bath packed in sawdust in a large light-proof box provided with a window and sliding shutter. Each cell was in a separate stall. A shielded cable ran from the cell-box to a selector panel by which any cell could be connected to the measuring apparatus. A 1000-watt lamp was used as the light source and the light was concentrated upon the cell under test by means of a large glass lens. An x-ray tube was also available.

[11] Dufford, Nightingale, and Gaddum, Jour. Am. Chem. Soc. **49,** 1858 (1927).

[12] R. T. Dufford, Jour. Opt. Soc. Amer. **18,** 17 (1929) and R. T. Dufford, Phys. Rev. **33** 119 (1929).

[13] N. W. Kondyrew, Ber. D. Deutsch. Chem. Gesell. **58,** 464 (1925).

A Leeds and Northrup potentiometer, type 7651, was used for e.m.f. measurements and the slide-wire of the same instrument with extensions for the ratio-arms of the bridge. A microphone hummer and a tuned vacuum-tube oscillator gave 1000-cycle current for the bridge. The oscillators were remote from the bridge and current was brought up by a shielded cable. The bridge circuit was that described by Jones and Josephs[14], but a two-mf mica condenser was connected in series with the cell to prevent the possibility of polarization. Without this precaution, it was found that resistance and e.m.f. changed so rapidly under test conditions that measurements were meaningless. A diagram of the bridge is shown in Fig. 1.

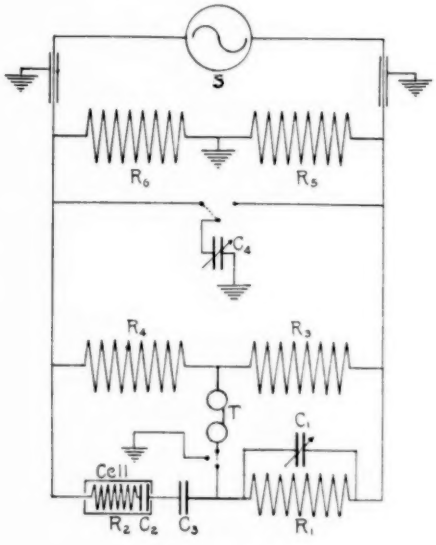


Fig. 1. Diagram of bridge circuit.

The theory of this bridge is the same as that given by Jones and Josephs with the insertion of the capacitance of the condenser mentioned above. In order to balance this bridge, two conditions must be fulfilled, as follows:

$$R_2 = \frac{R_1 R_4}{R_3}\left[\frac{1}{1 + R_1^2 C_1^2 \omega^2}\right] \tag{1}$$

$$C_2 = \frac{C_3(R_1^2 C_1^2 \omega^2 + 1)}{R_1^2 C_1 \omega^2 (C_3 - C_1) - 1}. \tag{2}$$

In these equations R_2 and C_2 are the resistance and capacitance of the cell, the capacitance being treated as in series with the resistance. R_3 and R_4 are the ratio-arms of the bridge, which were kept equal for the most part. C_3 is the capacitance of the condenser connected in series with the cell, and C_1 a variable capacitance in parallel with the known resistance R_1.

[14] Jones and Josephs, Jour. Amer. Chem. Soc. **50,** 1049 (1928).

The other resistances and capacitances are parts of the modified Wagner ground. The parenthetical correction factor in Eq. (1) is usually near enough to unity to be safely neglected, but in some of the cells tested here it was found to be as low as 0.75. Eq. (2) made possible the computation of the cell capacitance from data obtained during the measurement of the cell resistance. It can be seen that the balance conditions are functions of the frequency of the bridge current. Since the oscillators both gave out several harmonics, it was never possible to obtain complete silence in the phones, but merely to balance out the fundamental.

A number of tests were made which indicated that the resistance measured by the bridge was the electrolytic resistance and was very slightly affected, if at all, by films on the electrodes. For example, tests showed that variations of the distance between electrodes produced proportional changes in the resistance.

When an approximate value of the cell-resistance was known, bridge readings could be taken every minute. Potentiometer readings were taken at one-minute or half-minute intervals. Usually cells were illuminated for five minutes and then allowed to remain dark for an equal period.

The tests made can be classified under four general headings, which will be discussed in turn.

(a) *The effects of illumination and mechanical agitation on e.m.f.* Every cell was tested in this way. Ordinarily the entire cell was illuminated. With H-cells, tests were also made by illuminating separate electrodes or the cross-bar. In a few cases, a slit was placed in front of a straight cell so that a narrow ribbon of light passed parallel to the electrode surface or merely through the solution. Tests were made with varying degrees of mechanical agitation. As most of this part of the work was a repetition of what had been done by others, only the general conclusions will be given.

The e.m.f. was greatly affected by agitation of the cell and by polarization. The photovoltaic effects occurred without noticeable temperature changes. Oscillations of e.m.f., due to some unknown cause, took place even in the dark. Any change in the electrode surface caused an e.m.f. change, for example, exposing the electrode to air for a moment, cleaning the surface, etc. E.m.f. changed with age of the cell, partly because of concentration changes and partly no doubt because of slow electrolysis by minute leakage currents. Cells sealed in glass retained properties for many months but the e.m.f. varied and also the magnitude of the photovoltaic response. Light affected the potential of a given electrode almost invariably in the same way. Illumination of the electrolyte alone produced very small effects, possibly due to scattered light reaching the electrodes. In a few cases readings closely spaced showed that the light-e.m.f. effect involved two or three successive alterations. These were shown, by illuminating first one electrode and then the other by means of the narrow slit, to take place part near one electrode and part near the other, but very little, if any, in the body of the liquid. These tests, in general, favored the belief that the voltage phenomena are mainly localized near the electrodes. As a whole, these

conclusions are in agreement with those given in papers by the writer's colleague, R. T. Dufford, already quoted[11,12] or soon to be published.

(b) *Measurements of e.m.f. as affected by irradiation with x-rays.* The general results obtained upon exposing certain cells to a beam of x-rays have already been reported in a brief note.[15] Although they gave some promise as a means of measuring x-ray intensities, there were uncertainties about their behavior which need clearing up. This x-ray response differed from that produced by visible light in magnitude and frequently in sign, indicating that it was a different sort of action. Fig. 2 is a typical graph.

(c) *Measurements of e.m.f., resistance, and capacitance of cells as affected by visible light or by x-rays.* The accuracy of resistance measurements was about 0.1 percent, while that of the capacitance measurements was about

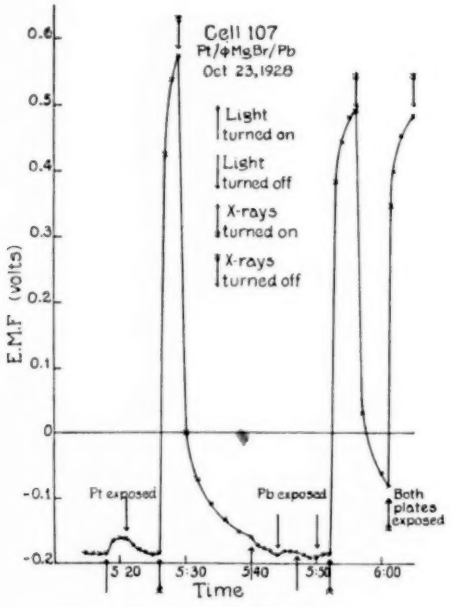


Fig. 2. E.m.f. as affected by light and x-ray illumination.

1 percent. Values of the cell-capacitances found by this bridge agreed with those indicated by a Leeds and Northrup Farad Bridge. All the cells studied carefully were of the test-tube type with electrodes about 5 mm apart. Platinum electrodes were of 1 cm^2 area, most of the others were of 5 cm^2 area. Resistance of a cell ranged between 500 and 20,000 ohms, capacitance from 0.4 to 35 mf.

Seven cells contained phenylmagnesium bromide with various electrode combinations. None of these cells showed any change in resistance upon exposure to light when the cells were new, but one, with platinum and copper electrodes, developed such sensitivity after about six months. The light-induced change was a drop of about 1 percent in resistance, recovery taking

[15] R. T. Dufford and H. E. Hammond, Phys. Rev. **33,** 124 (1929).

place in an equal period. Temperature rise produced an increased resistance which persisted as long as the cell was observed, indicating that the light effect was a different phenomenon.

Two cells filled with ethylmagnesium iodide gave no definite light-resistance response.

Four cells contained ethylmagnesium bromide. These were all symmetrical cells with electrodes of aluminum, platinum, copper, and sodium respectively. These cells showed lower resistances than those containing phenylmagnesium bromide. The resistances decreased and the capacitances increased with age in general. A single cell with platinum and aluminum electrodes and containing bromo-ethylmagnesium bromide showed a high

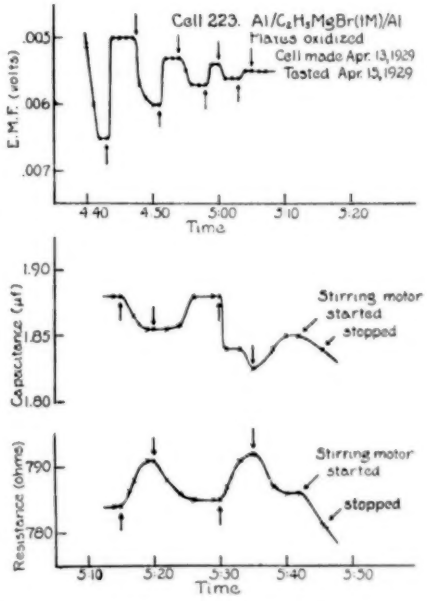
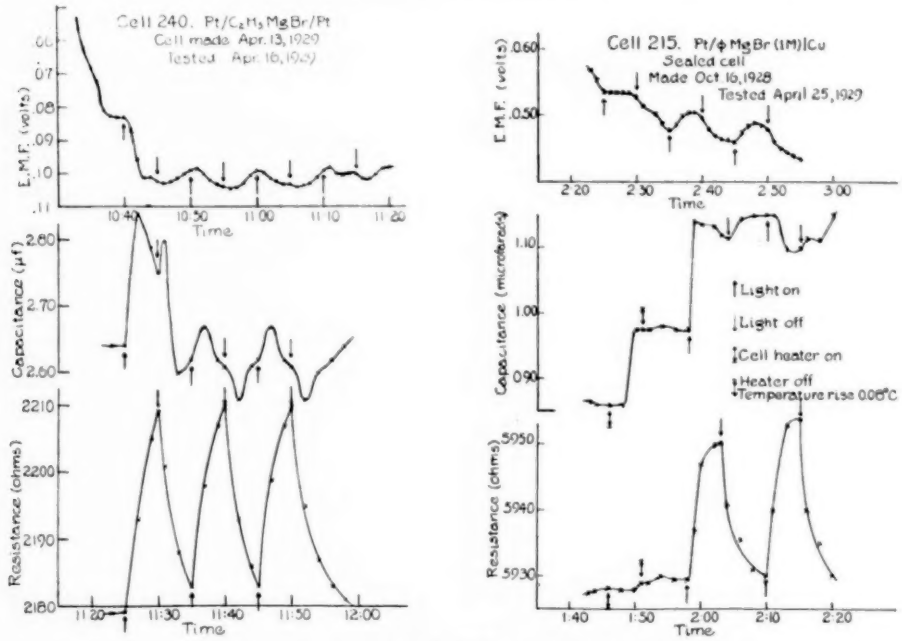


Fig. 3. Effect of light on e.m.f., resistance and capacitance. Upward-pointing arrows indicate when light was turned on; downward-pointing arrows when light was turned off. The same notation is followed in succeeding figures.

initial resistance, which became smaller with age, while the capacitance increased. All these cells showed an increase of about 1 or 2 percent in resistance during five minutes illumination, followed by recovery in an equal period of darkness. The changes in resistance could be detected within a few seconds after turning on or off the light. Resistance changes due to temperature rise could not be detected so soon and the changed value usually persisted after the temperature had come back to the original level. Furthermore, these light-induced changes were not in the same sense as those due to temperature rise in all cases. Figs. 3, 4, and 5 show typical sets of results. It was not possible to trace any general interrelation between the changes in e.m.f., resistance, and capacitance when the cells were illuminated. Fig. 4 shows the only example found of any apparent regular relation between

the capacitance values and the presence or absence of light on the cell. This relation existed for only a part of the test, as can be seen.

No tests of specific resistance were made for the Grignard solutions, but the values must be high in view of the high resistances compared with the cell dimensions. Secular variations in resistance ran as high as 50 or 60 percent, while the light-induced changes never exceeded 2 percent. The former changes were not reversible, the latter were. The photoelectric hypothesis is not tenable as some of the light-induced changes were increases in resistance. Neither does it seem reasonable to attribute a voltage variation of from 10 to 50 percent to a process which caused a resistance change of only 1 or 2 percent. The secular changes in resistance were undoubtedly due to chemical changes in the cell composition, evidences of which sometimes be-



Figs. 4 and 5. Effect of light on e.m.f., resistance, and capacitance.

came evident to the eye as time went on. The writer believes that the light-induced resistance changes were due to temporary and reversible variations in solvation of the ions rather than in percentage of ionization. These data, therefore, served to strengthen the idea that the voltage phenomena are due to changes near the plate surfaces, but the lack of any consistent relation between the capacitance changes and the presence or absence of light did not give any definite evidence to locate the seat of action on the surface itself.

Operation of the x-ray apparatus caused so much noise in the phones that the bridge could not be balanced while the cell was being irradiated. If the resistance or capacitance was affected by x-rays, the effect did not persist long enough to be measured after the apparatus was shut off.

As the high-frequency bridge current sometimes altered the e.m.f. of the cells, the potentiometer tests were always made first and the bridge measurements as soon as possible thereafter.

(d) The development of light-resistance sensitivity in one phenylmagnesium bromide cell after several months suggested that electrolysis of these cells might yield some interesting results. The high values of the capacitance per unit area in several of the cells also increased the belief that interesting data of that sort might be found by an application of the electrolytic or "forming" process. Although this feature was not a part of the program originally outlined, it was hoped that something bearing on the general question might be developed.

Electrolysis of ether solutions shows some features not common to aqueous solution. Ollar[16] showed that in certain cases hydrogen was evolved at both electrodes, but he offered no explanation. Only a few papers[17] have yet been published upon the electrolysis of Grignard reagents but work along that line is now being done. It is not possible to say just what happened in the cells treated in this paper, except that in some cases magnesium in the "tree" form was deposited on the cathode. Most of the deposit fell off the plate as soon as the current ceased, but the plate area may have been increased enough to account for at least a part of the increase in capacitance always noted. Luminescence has been observed during electrolysis, sometimes on the anode, sometimes on the cathode, sometimes on both plates.

In the electrolysis, a current of a few milliamperes at 15 volts was passed for 15 minutes through the phenylmagnesium bromide cells in the same direction as the current they generated. With the lower-resistance ethylmagnesium bromide cells 5 volts was applied for 5 minutes. With the first-mentioned type, the process resulted uniformly in decreased resistance, increased capacitance, and a light-resistance sensitivity where none had existed before. In the presence of light a decrease in resistance took place, while in a period of darkness equal to that of the illumination the original resistance was recovered. The ethylmagnesium bromide cells all developed capacitances 2 to 6 times the former values, but the resistance varied differently in different cells. No special change in light-resistance sensitivity was observed, except a small diminution in the magnitude.

Figs. 6 and 7 show results of tests with one cell of each type. Again no general relation was found between e.m.f., resistance, and capacitance changes under illumination. No resistance or capacitance effects were noted under x-ray irradiation.

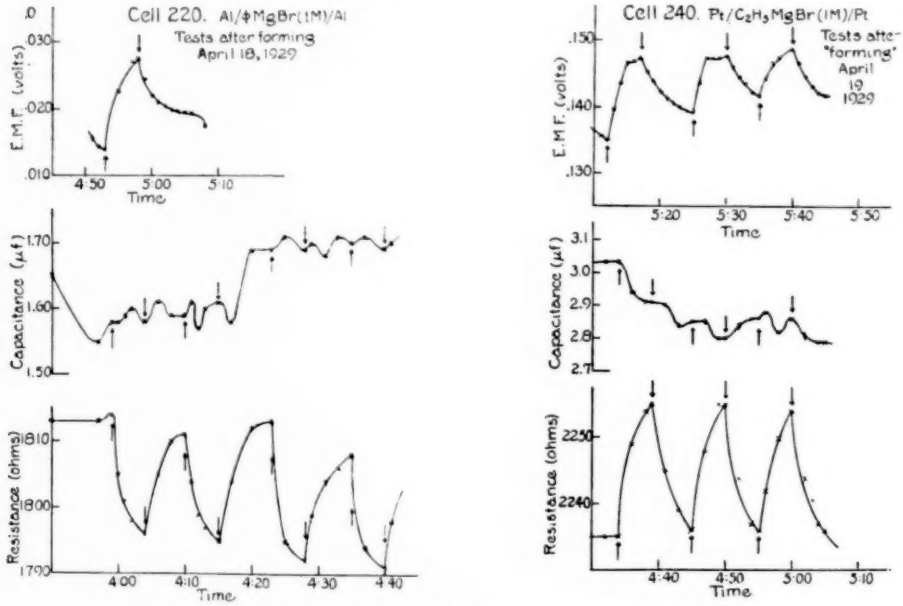
In several cases, cells measured with an ordinary d.c. Wheatstone bridge showed asymmetrical resistances somewhat like those shown by aluminum rectifiers, but the asymmetry was not so pronounced. In one case, the resistances to currents in opposite directions were 8000 and 16000 ohms respectively, while in another the figures were 2600 and 19000 ohms, the higher resistance being uniformly offered to a current opposite to the "forming"

[16] A. Ollar, Thesis, University of Missouri (1926).

[17] L. W. Gaddum and H. E. French, Jour. Am. Chem. Soc. **49**, 1295 (1927).

current. The aluminum rectifier stops a current flowing in the same direction as the forming current. The cells which showed this characteristic had aluminum plates and contained phenylmagnesium bromide. Such differences of resistance are not great enough to be of practical use.

One other interesting point remains to be discussed, but lack of exact knowledge of the chemistry of these cells forces rather vague conclusions. Films on aluminum in electrolytic condensers have been found to have thicknesses ranging from 10^{-2} to 5×10^{-6} cm and the dielectric constant was estimated as 14.5.[18] Assuming a value of 1 for the dielectric constant in the present cases, film thicknesses have been computed for two cells which showed very large capacitances. An ethylmagnesium bromide cell gave over 7 mf per cm² after "forming". For $k=1$, the film thickness was 1.2×10^{-8}



Figs. 6 and 7. Effect of light on e.m.f., resistance and capacitance.

cm. A phenylmagnesium bromide cell with copper plates showed about the same capacitance per unit area and the thickness figures were 8×10^{-8} cm. These figures are of the order of interplane distances in crystals, so it is possible that the films are single layers of molecules or a few such layers. It may be noted that the thickness attributed to the film in phenylmagnesium bromide, a benzene-ring compound, is greater than that found for ethylmagnesium bromide, a short-chain compound, as might be expected. The very large capacitance per unit area, 7 mf per cm², is worthy of note. If these thickness figures are near the truth, it seems strange that regular light-capacitance effects were not found, especially in view of the fact that other evidence seems to indicate that the photovoltaic effect is dependent upon condition of the electrode surface.

[18] H. O. Siegmund, Trans. Am. Elect. Chem. Soc. **53,** 203 (1928).

The following conclusions may be drawn.

(a) The conclusions of others as to variations in the e.m.f. of Grignard cells with age, with mechanical agitation, and with illumination are corroborated. The evidence seems to locate the seat of the phenomena at or near the surfaces of the electrodes.

(b) Several types of cells gave large voltage responses when exposed to x-rays and also showed large changes in current through a high-resistance circuit during such irradiation. The phenomenon is apparently a different one from the photovoltaic effect in the same cells.

(c) The resistance and polarization capacitance of a number of cells have been measured by means of a high-frequency bridge. Cells containing phenylmagnesium bromide showed no light-resistance response when freshly made, some containing ethylmagnesium bromide and one containing bromoethylmagnesium bromide did. This has been shown not to be a temperature effect. Some cells showed an increase of 1 or 2 percent in resistance when illuminated and some a decrease of about the same percentage, but a given cell was consistent. These results made a general photoelectric theory untenable and also indicated that the rather large voltage variations were not of the same origin as the resistance changes. The small reversible changes in conductivity were laid to alterations in solvation of the ions rather than to changes in ionization percentage. Such capacitance changes as were found seemed unrelated to other phenomena.

(d) A "forming" or electrolytic process was carried out with several cells containing phenylmagnesium bromide and ethylmagnesium bromide. The former then showed a light-resistance sensitivity. After the process, larger capacitances were observed in all cases, but no regular light-capacitance response.

Asymmetrical resistances, smaller than those in aluminum rectifiers, were found in a few cells.

Capacitances as high as 7 mf per cm^2 were found. Assuming a value of unity for the dielectric constant of the films, the probable thickness of the films was estimated to be of the order of the diameter of a molecule or a small multiple of that diameter. The thickness was greater for a benzene-ring compound than for the short-chain compounds used.

No effects on resistance or capacitance due to x-ray irradiation were detected.

In general, the evidence supports the belief that the voltage variations with illumination must be attributed to phenomena near enough to the electrodes to be affected by changes on their surfaces. The capacitance effects were inconclusive as to whether light-induced effects occurred in the films.

The writer expresses his sincere gratitude to Mr. R. T. Dufford, at whose suggestion the investigation was attempted and whose assistance and advice have been invaluable in carrying out the work; also to Professor O. M. Stewart for suggestions as to the bridge circuit and for the provision of the necessary apparatus and materials.

THERMAL CONVECTION

By R. W. Babcock
De Pauw University, Greencastle, Indiana

(Received March 8, 1930)

Abstract

The differential equations which apply to slow steady convective motion of a viscous fluid are the standard equations of hydrodynamical theory, combined with equations expressing the law of thermal interchanges in a moving fluid. Approximate solutions are found following the method outlined by Oberbeck (Ann. d. Physik, 1879, p. 271). A comparative study of the exact solution of a special system of non-linear ordinary equations and the Oberbeck approximate solution shows that the magnitude of the constants in the system controls the rate of convergence of the approximation, and often produces divergence. Solutions with graphs of temperature and velocity fields have been computed for special cases of cylindrical and plane boundaries with sinusoidal impressed boundary temperatures. If this temperature has a vertical gradient only, the Oberbeck method produces a null solution, corresponding to equilibrium in stratified layers. Arithmetical solutions for common liquids at ordinary temperatures show that the Oberbeck solutions diverge unless the gradient is much too small to be easily applied in laboratory practice.

ANALYTIC solution of the problems of convection in fluids presents extreme difficulty. No methods have been devised for the exact solution of the differential equations, which are non-linear, and must be solved subject to complicated boundary conditions.

Free convection in a fluid consists of the motions produced by gravity throughout its volume due to changes in its density caused by variations in temperature. This paper presents approximate solutions of certain special cases of steady free convection, produced by temperature differences maintained at the fixed boundaries of the fluid.

If expressions are formed to represent: (1) the flow of momentum; (2) the flow of mass; (3) the flow of energy throughout any volume chosen in the fluid, and terms of second order are neglected, the resulting equations are

$$(dV/dt) - \alpha gT + (1/\rho)\nabla p - \nu\nabla^2 V = 0, \tag{1}$$

$$\text{div } V - \alpha dT/dt = 0, \tag{2}$$

$$(dT/dt) - h^2\nabla^2 T = 0. \tag{3}$$

The symbol g denotes a vector of magnitude $|g| = 32.2$ ft/sec.^{2} whose direction is upward.

The simplest cases are the flow of a liquid between two infinite parallel plane plates (Fig. 1), and between two infinitely long vertical concentric circular cylindrical pipes (Fig. 2). In both of these cases, the velocity equation reduces to $\nabla^4 u = 0$, and the temperature equation to

$$\alpha gT + \nu\nabla^2 u = 0. \tag{4}$$

When temperatures $\pm t$ are maintained on the plane plates, whose equations are $y = \pm a$, the solutions are

$$u = -\frac{\alpha g t}{6a\nu}(y^3 - a^2 y), \tag{5}$$

$$T = ty/a. \tag{6}$$

For the cylinders whose radii are 1 and e, upon whose boundaries are maintained temperatures respectively of 0 and 0.5, the solutions are (using the physical constants of water)

$$u = 4.126[r^2 - 1 - \log r(1.849 - 0.615r^2)], \tag{7}$$

$$T = 0.5 \log r. \tag{8}$$

In both these cases, it is seen that the temperature is exactly what would be produced by conduction alone in a rigid body filling the space now occupied by the flowing liquid and having the same physical constants.

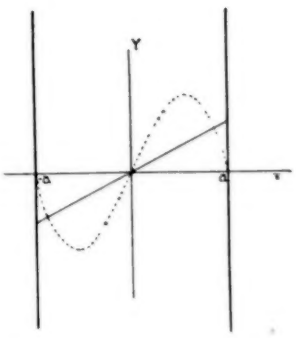


Fig. 1. T, solid curve; u, dotted curve.

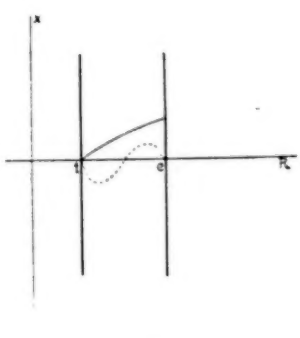


Fig. 2. T, solid curve; u, dotted curve.

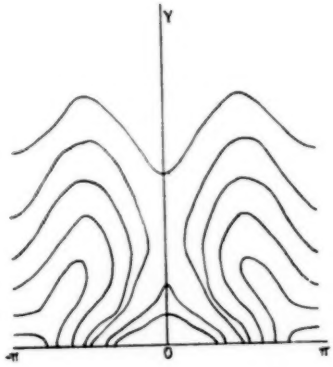


Fig. 3. Temperature field and isothermal lines.

For the solution of other cases, this paper follows the rule for approximation of such equations which was developed by Oberbeck.[1] This method reduces the analysis to equations of the type $\nabla^2 f(x, y, z) = F(x, y, z)$ subject to proper boundary conditions. Oberbeck, in his paper, starts the approximate analytic solution of the convection of a liquid between two concentric spherical shells, which are maintained at different constant temperatures, computing the first velocity terms and the second temperature term. He does not consider conditions of convergence of the solution.

To check Oberbeck's method of solution, a pair of similar simultaneous ordinary differential equations,

$$\frac{d^2\Psi}{dx^2} - a\frac{dT}{dx} = 0, \tag{9}$$

$$\frac{d^2T}{dx^2} - b\frac{dT}{dx}\cdot\frac{d\Psi}{dx} = 0, \tag{10}$$

[1] Oberbeck, Ann. d. Physik, 1879, S 271.

may be solved and the results computed numerically for various values assigned to a and b. The exact solution, subject to boundary values, $T(0) = -\alpha$, $T(l) = \alpha$, $\Psi(0) = \Psi(l) = 0$, is

$$\Psi = \frac{2}{b} \log \left[\cos \frac{Bl}{2} \sec B\left(x - \frac{l}{2} \right) \right], \tag{11}$$

$$T = \frac{2B}{ab} \tan B\left(x - \frac{l}{2} \right), \tag{12}$$

where B is the first positive root of the transcendental equation $B \tan (Bl/2) - (ab/2) = 0$. For $\alpha abl^{-1} = 0.25$, the Oberbeck type of series approximations converge rapidly toward the Maclaurin expansions of the exact solution; for $\alpha abl^{-1} = 1$, the convergence is slow; and for $\alpha abl^{-1} = 5$, divergence of the series is obtained. Any approximation, therefore, to equations of type of Eqs. (1), (2), (3), must depend for their convergence upon the values of their physical constants. Since these are restricted in a problem involving laboratory experiments, the analytical question of convergence prescribes the amount of temperature difference which may be applied. In the numerical computation of the following cases, the physical constants of glycerine have been chosen. These examples have been set up so that the Z-axis is a line of symmetry, and all the equations have but two independent variables.

Whenever the liquid is assumed to be absolutely incompressible so that div $V = 0$, and cartesian coordinates are used, a "current function" Ψ is formed such that

$$u = \partial\Psi/\partial y, \qquad v = -\partial\psi/\partial x. \tag{13}$$

Eqs. (1), (2), (3), then become

$$h^2\nabla^2 T = \frac{\partial T}{\partial x}\frac{\partial \Psi}{\partial y} - \frac{\partial T}{\partial y}\frac{\partial \Psi}{\partial x}, \tag{14}$$

$$\nabla^4 \Psi = \frac{\alpha g}{\nu}\frac{\partial T}{\partial x}, \tag{15}$$

subject to $\Psi = \partial\Psi/\partial n = 0$, and $T = T(x, y)$ at the boundary surfaces. Two such cases are studied in detail.

(A) A half-space above the plane $y = 0$ upon whose surface $T(x, y) = t \cos x$ is maintained. The following solutions are obtained:

$$T = te^{-y} \cos x + \frac{\alpha g t^2}{128 h^2 \nu}\left[2 + e^{-2y}\left\{(2y^2 + y)\cos 2x - (4y^2 + 4y + 2)\right\}\right] \tag{16}$$

$$\Psi = -\frac{\alpha g t}{8\nu} y^2 e^{-y} \sin x - \frac{\alpha^2 g^2 t^2}{24576 h^2 \nu^2} e^{-2y} \sin 2x (4y^4 + 4y^3 + 3y^2). \tag{17}$$

The temperature and velocity fields are shown in Figs. 3 and 4. The limiting temperature approached high up in the space is not zero, but a definite positive value, $\alpha g t^2/64 h^2 \nu$, the heat having been carried upward by the convection currents and not brought down again as rapidly.

(B) The space between two infinite horizontal plane plates whose equations are $y = \pm l$, upon both of which $T(x, y) = t \cos x$ is maintained. When l is chosen as 3, and t as 0.5, the principal temperature term is $0.0496 \cosh y \cos x$, and

$$u = -10^{-3} \sin x[0.28y^2 \sinh y - 1.08y \cosh y + 0.74 \sinh y], \quad (18)$$

$$v = 10^{-3} \cos x[0.28y^2 \cosh y - 1.64y \sinh y + 2.38 \cosh y]. \quad (19)$$

The temperature and velocity fields are shown in Figs. 5 and 6. In both these cases the velocity fields show a jet-like streaming above the warm portions of

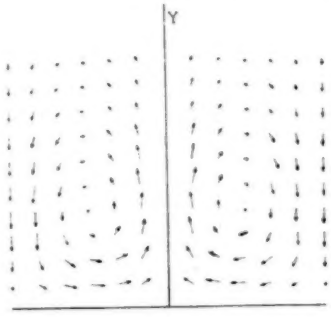


Fig. 4. Velocity field.

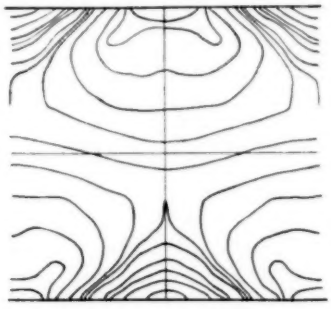


Fig. 5. Temperature field and isothermal lines.

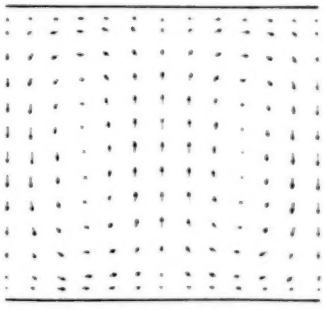


Fig. 6. Velocity field.

the boundary. This is of the same type as that observed by Nelson[2] in his experiments in convection. The boundary temperatures are different in his work, so that only a qualitative check is obtainable here.

Using polar coordinates, analytic solutions may be computed for impressed boundary temperatures more readily adaptable to laboratory conditions. In the following examples the container is assumed to be an infinite horizontal circular cylinder, the initial line chosen as the upward radius, the vectorial angle running counterclockwise. Eqs. (14) and (15) when transformed to this system of coordinates are

$$\frac{\partial T}{\partial \rho}\cdot\frac{\partial \Psi}{\rho \partial \theta} - \frac{\partial T}{\rho \partial \theta}\cdot\frac{\partial \Psi}{\partial \rho} = h^2 \nabla^2 T, \quad (20)$$

$$\nu \nabla^4 \Psi + \alpha g\left(\sin\theta \frac{\partial T}{\partial \rho} + \cos\theta \frac{\partial T}{\rho \partial \theta}\right) = 0, \quad (21)$$

[2] Nelson, Phys. Rev. **23**, 94 (1924).

where the radial and tangential components of velocity are

$$R = \partial\Psi/\rho\partial\theta, \qquad \Theta = -\partial\Psi/\partial\rho. \tag{22}$$

As usual, the boundary conditions prescribe the temperature maintained on the surface, and cause the velocity to vanish there.

(A) The first case discussed in this coordinate system is an impressed boundary temperature $T = t \sin\theta$. This may be considered as the temperature impressed in a large metal block, across which a linear horizontal temperature gradient is constantly maintained. Temperature within the block near the boundary has not been measurably changed by the convection within the cylinder.

The first approximation to the velocity is a pure rotation, the current function being

$$\Psi_1 = -\frac{\alpha g t}{64\nu}(1 - \rho^2)^2 \tag{23}$$

the same solution which was found by Love[3] in the deformation of a circular plate clamped at the circumference under uniform pressure. The temperature and velocity fields, approximated to another term, are shown in Figs. 7 and 8. This velocity field shows regions of "dead water" which have been observed under similar laboratory conditions.

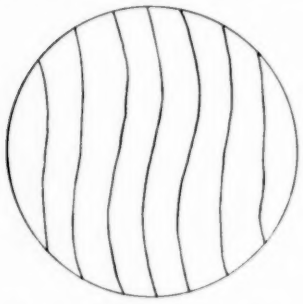


Fig. 7. Temperature field and isothermal lines.

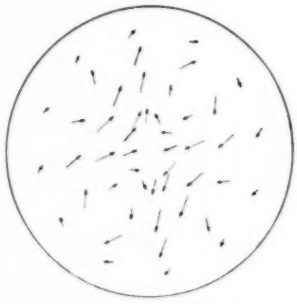


Fig. 8. Velocity field.

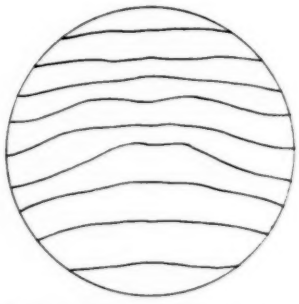


Fig. 9. Temperature field and isothermal lines.

For this case, a complete solution which does not include an assumption of the incompressibility of the liquid shows that the difference between the two types of solution consists of terms occurring only after the second approximations to temperature and velocity, and that these differences are of relative magnitude 10^{-3}. The analytic solution in this case is much more tedious. The values of the fluid pressure due to the convection current must be found, and the added accuracy of the solution occurs only in those terms which are of such size as to be entirely outside the range of experimental observation. The full solution is then neither a necessary nor an efficient method of attacking the problem.

(B) If a pure vertical gradient of any sort is impressed in the boundary temperatures, no motion is determined from the analytic solution. This represents equilibrium in the liquid, which is stable or unstable if the sign of the

[3] Love, Mathematical Theory of Elasticity, 3d ed., p. 490.

upward gradient is positive or negative. The body of liquid stratifies in horizontal layers. In order to consider an approximate solution, one of two choices must be made: (1) assume a form of initial velocity; (2) assume an initial temperature which does not have a pure vertical gradient such as $T_0 = (t\rho \cos\theta)/a + kf(\rho, \theta)$, where $f(a, \theta) = 0$ to satisfy the boundary conditions. Either of these choices is so arbitrary that the solutions obtained do not compare with facts which could be observed. Two choices for $f(\rho, \theta)$ are studied here, both of which have radial symmetry. These are (1) $f(\rho, \theta) = (kt/a)\,(a - \rho)$ and (2) $f(\rho, \theta) = (kt/a^2)\,(a^2 - \rho^2)$. The temperature and velocity fields are compared. The two sets are shown in Figs. 9, 10, 11, and 12. In both cases, the

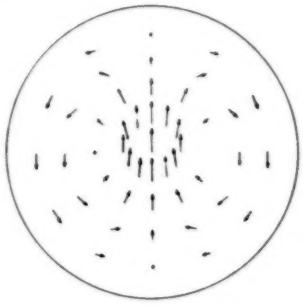


Fig. 10. Velocity field.

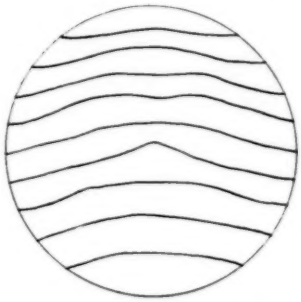


Fig. 11. Temperature field and isothermal lines.

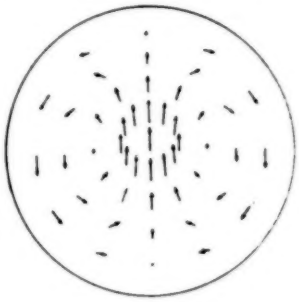


Fig. 12. Velocity field.

whole problem approaches a null solution as the parameter k is made infinitesimal, so that neither presents a satisfactory approximation to the desired result. There is, however, a tendency for the corrections to the temperatures to equalize and thus become independent of the specific form chosen for $f(\rho, \theta)$.

Since Eqs. (14) and (15) are non-linear, the sum or difference of two solutions is not a new solution. This prevents the use of the usual type of uniqueness proof to assume a second solution and show that the difference of the two solutions vanishes identically. The essential accuracy of the approximations must be checked through experiment.

In all the particular examples studied, it is, of course, necessary to study carefully the question of the convergence of the series obtained:

$$T = T_0 + \alpha T_1 + \alpha^2 T_2 + \cdots, \tag{24}$$

$$\Psi = \alpha\Psi_1 + \alpha^2\Psi_2 + \cdots. \tag{25}$$

For a liquid having a low viscosity, like alcohol or water, the sufficient condition for convergence requires the amplitude of the impressed temperature not to exceed about 10^{-4} degrees per centimeter of the horizontal cylinder. Such values are useless for comparison with any type of experiment. For a much more viscous liquid, such as glycerine, the amplitude of the impressed temperature may be as large as 10^{-1} degrees per centimeter radius. Even this restricts the usefulness of the Oberbeck method to such an extent as to render it practically useless as a comparison with laboratory results. The computations here show the dependence of the analytic solution upon the physical constants of the particular problem. They also determine the small amount of error obtained by assuming the absolute incompressibility of the liquid and demonstrate the fact that these corrections may be neglected, thus materially shortening the computations, which are laborious under the most favorable conditions.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

*On the Mechanism of "Atomization"

So far as the writer knows no adequate explanation has been offered of the phenomenon of liquid "atomization." Scheubel[1] has, indeed, given some interesting and instructive spark pictures of the process as it occurs in the carburetor throat, but not much direct information can be derived from them except at fairly low air speeds. The fact, however, that the phenomenon can be used with confidence in the design of many machine elements,—that certain results may be expected to attend certain conditions,—is tacit declaration that the process has a definite physical background.

If, given a quantity of liquid which at one time exists as a single comparatively large mass, and a moment later is observed to be in the form of a very great number of very small discrete drops, we merely make the assumption that there must be an intermediate stage in which fine ligaments are formed, of such diameter that they will disintegrate into drops of the observed size, we can account for this phenomenon on the basis of Rayleigh's theory of jet disintegration and certain recent observations of the size of the drops formed when a liquid is atomized. This assumption seems reasonable, since time and temperature considerations exclude the possibility of evaporation and subsequent recondensation; it seems necessary, since it will appear very improbable that the existence of such fine ligaments can ever be directly demonstrated; and it is hoped to show that it is sufficient.

Rayleigh[2] thus explained the disintegration of a jet which we shall identify with the ligament mentioned in the preceding paragraph: He considered the jet as an infinitely long cylinder of liquid initially in equilibrium under the influence of the tension of its envelope, and investigated the efficiency of various types of disturbance in upsetting this equilibrium. He found that

$$\alpha=\alpha_0 e^{qt} \tag{1}$$

where α and α_0 are amplitudes, at times t and 0, respectively, of a disturbance symmetrical with reference to the cylinder axis; e is the Napierian base; and

$$q=\left(\frac{8T}{\rho D^3}\right)^{\frac{1}{2}}\cdot F \tag{2}$$

In Eq. (2), T and ρ represent the liquid's surface tension and density, respectively: D is the diameter of the undisturbed filament; and F is a (dimensionless) function of Z, the ratio length/diameter. The denominator of this fraction is the same as D above, while its numerator is the distance along the jet between two adjacent points in the same phase of vibration.

When α grows to $D/2$ the filament breaks.

The function F has been investigated by Rayleigh[2] and by the present writer.[3] As a result it follows that the effective value of F may be taken as about 0.34 at $Z=4.5$. For this value of Z it also follows that the diameter d of a spherical drop will be about twice D, the diameter of the cylindrical segment from which the drop is formed.

Hausser and Strobl[4] and Sauter[5] found,

* Publication approved by the Director of the Bureau of Standards of the U.S. Department of Commerce.

[1] F. N. Scheubel, Jahrbuch der W. G. L. p. 140 (1927).

[2] Rayleigh, Proc. Lon. Math. Soc. **10,** 4, (1879).

[3] Castleman, Nature **114,** 857, (1924).

[4] Hausser and Strobl, Zeits. tech. Phys. **5,** 154 (1924).

[5] J. Sauter, Zeits. V.D.I. **72,** 1572 (1928).

for water atomized in a high speed air stream, a mean value of d of about 6×10^{-4} cm, while Woltjen[6] found about the same for oil atomized by "airless" injection into a high pressure bomb. Taking 10^{-3} cm as an upper limit, we have 5×10^{-4} cm for D, so that Eq. (2) gives $q=740{,}000$ sec.$^{-1}$ for water atomized in a high speed air stream.

Now, it is very difficult, if not impossible, to estimate the value of α_0 precisely. The molecular diameter is, however, of the order of 10^{-7} cm[7] so it seems legitimate to place about 10^{-8} cm as a lower limit. To cut through a ligament 5×10^{-4} cm in diameter, α must grow to $D/2=2.5\times10^{-4}$ cm. The necessary time is, by Eq. (1), $t=(1/q)\ln\alpha/\alpha_0=(1/M_q)\log_{10}\alpha/\alpha_0=1/73{,}000$ sec. (approx.). This would correspond to a motion of about 2 millimeters of the *air* stream in the throat of the carburetor of an automobile engine turning over at high speed; or of about 1 mm of the spray 0.0005 sec. after injection at 8000 lbs/in^2, into a chamber held at 200 lbs/in^2 (N.A.C.A. Report #268).

The above gives *upper* limits of the possible lengths of these fine ligaments. Small wonder that they have never been observed!

R. A. Castleman, Jr.

Bureau of Standards,
March 15, 1930.

[6] Woltjen, Dissertation, Tech. H.S. at Darmstadt (1925) (Data taken from N.A.C.A. Tech. Memo. #403, pp. 19–22).

[7] Rayleigh, Phil. Mag. **48,** 331 (1899).

The Atomic Weights of Hydrogen and Helium.

Eddington (Proc. Roy. Soc. **A126,** 696, 1930) has obtained a new theoretical value of 1/137 for the fine structure constant α. This agrees much better with observational data than his previous value of 1/136. He also reaches the very interesting conclusion that in a *rigid system* of protons and electrons, there should be a proportional loss of mass equal to α. The most rigid system of this kind now known is the alpha-particle, and the loss of mass, assuming the alpha-particle to be absolutely rigid, agrees more closely with the theory than is indicated in Eddington's paper. In fact, on this assumption, an atomic weight of 1.00777 ± 0.00002 for hydrogen (see Birge, Phys. Rev. Suppl. **1,** 1, 1929) leads to 4.00166 as the calculated atomic weight of helium. As I have noted (footnote 12a, page 21, loc. cit.) the best chemical value for this latter quantity is now 4.0018. Because of the newly discovered isotopes of oxygen, Aston's mass spectrograph value of 4.0022 should be lowered about one part in 10,000 (page 69, loc. cit.) and then agrees precisely with the chemical value. Hence the observed and calculated values of the atomic weight of helium differ by only one part in 30,000, and this may be taken to indicate that the alpha-particle is in fact very nearly "rigid."

This correlation of the fine structure constant with the "packing effect" in an alpha-particle has already been suggested, on a purely empirical basis, by Lunn (Phys. Rev. **20,** 1, 1922) and has been revived by Witmer (Nature **124,** 180, 1929). In this earlier work, the predicted decrease in mass was given as $\alpha/(1+\alpha)$, but this differs by an entirely negligible amount from the present predicted decrease of α.

If the nucleus of the isotope oxygen "16" is a non-rigid system composed of four such "rigid" alpha-particles, the mass of this nucleus should be four times the mass of an alpha-particle, diminished by the mass-equivalent of the binding energy of the four alpha-particles. The atomic weight of the isotope oxygen "16" is 15.9984 (one part in 10,000 less than 16.0000), and one thus obtains 0.0082 atomic weight units (or one part in 1950 of the total mass) as the mass-equivalent of the binding energy. This seems to be a reasonable value.

Raymond T. Birge

University of California,
March 25, 1930.

A New Unified Field Theory and Wave Mechanics

In your issue of January 1st 1930, you published a preliminary notice of a paper on the above subject by the present writer. A few more words of explanation thereof, not included in the paper itself seem called for.

The fundamental postulate is that the unobservable is non-existent. This is familiar in wave mechanics, but is now applied for the first time to relativity.

Since the metric tensor of space time is

defined logically in terms of an unobservable N-dimensional psuedo-Euclidean space, for classical relativity, by our postulate the definition is impossible. For us the metric tensor becomes a perfectly arbitrary set of ten functions of the space-time coordinates, available for descriptive purposes. The old analogy with the intrinsic properties of two-dimensional curved surfaces can be dropped and surpassed. The metric tensor is defined only by transfer according to a certain rule from an initial point, and its increments are not perfect differentials; it depends upon the track along which the rule has been applied. Such a tensor is sufficient to give definite magnitude to the elements of the vector lines in the vector field defined by another transfer rule applied to a vector. As already pointed out these vector lines become the known orbit equations when the simplest derivable definite tensor function is used to describe the electric field.

This is a distinct improvement on the theory of Kaluza and Klein which introduces an unknowable fifth dimension directly into the equations, apart from the others required for the logical definition of the metric.

It has been found necessary to abandon the hope that the theory might lead to quantised orbits round atomic nuclei; but this is not necessary, for there is no longer any inconsistency with wave mechanics. Thus classical electromagnetic theory was based on the concept of a local singularity with definite position and velocity; but no such singularity is at the basis of the present theory. The new point of view is this: If local singularities exist, then their tracks can be described by means of the vector line theory, but if the uncertainty in the position or velocity of such singularities becomes significant, the method will no longer be useful, and statistical methods appropriate to the case must be used. There is thus no longer any inconsistency, it is merely a matter of convenience in description.

We may finally claim to have cleared up the apparent inconsistencies between the field theory and the atomic theory, and set the former on the same satisfactory philosophical basis as the latter.

WILLIAM BAND

Yenching University,
Peping, China,
February 28, 1930.

The Carbon Dioxide Theory of the Ice Ages

It was pointed out long ago by Tyndall, (Phil. Mag. **22,** 277 (1861)), that changes in the carbon dioxide content of the atmosphere might be a controlling factor in the cause of ice ages. The suggestion was generally accepted for many years but more recently writers have denied its importance, for example Angström, Ann. d. Physik **6.** 172 (1901), Humphreys, ("Physics of the Air," pages 564 and 602 (1929)), Abbot and Foule, (Smithsonian Institution, Annals Astrophys. Obs. **2,** 172 (1908)), Jeffreys. ("The Earth," page 263 (1924)) and Simpson (Nature **124,** 988 (1929)) and "Past Climates," page 9 (1929)). These writers have used the single blanket argument, which in its simplest form may be stated as follows: If all the energy leaving a hot body is absorbed by one blanket the cooling rate will not be reduced by increasing the number of blankets. Since water vapor is practically completely absorbant for the radiation in the CO_2 absorption bands, they argued that changing the amount of CO_2 in the atmosphere would not affect the climate of the earth.

The argument of course is not correct. For example, the temperature T degrees Kelvin of a body warmed by a constant supply of energy f ergs cm^{-2} sec^{-1} and cooled by radiation through an absorbing sheath containing n molecules, in a 1 cm^2 column through the sheath, of atomic absorption coefficient α for the radiation, is given by

$$T^4 = f(1+\alpha n)/a\sigma, \qquad (1)$$

where a is the absorption coefficient of the surface of the body and σ is the Stefan-Boltzmann constant. From (1) it is seen that T increases with n for all values of n. Calculations for the carbon dioxide and the water vapor in the upper atmosphere, using (1) and taking into account the shift of the spectral distribution curve of the radiation as it passes through the atmosphere, etc., show that a 70 percent decrease in the carbon dioxide will cause a decrease of more than 6 percent in the radiation entering the lower atmosphere, (Terr. Mag. and Atmos. Elec.

33, 253 (1928)). This decrease alone will account for a temperature drop of about 6°C at the earth's surface. When to this 6° is added decreases associated with decreased humidity, decreased wind action in providing a cooled insulating layer and increased reflection of sun's rays accompanying the extension of ice fields we would expect a temperature drop such as would be associated with an ice age. It is hoped to develop these ideas to some extent in a future paper.

H. B. MARIS

Naval Research Laboratory,
March 31, 1930.

BOOK REVIEWS

Magnetism. EDMUND C. STONER. viii+117 pp. 20 figs. E. P. Dutton and Co., New York 1930. Price: $1.10.

This little book is one of a series by English physicists which propose to supply the advanced student of physics in general with condensed accounts of recent progress in specialized branches of his subject. The general preface by O. W. Richardson emphasizes the utility of these monographs to those preparing for examinations. The present exemplar is well written and is thoroughly up-to-date in all that relates to the theory of magnetism and to the experimental basis upon which it rests, that is to theory and experiment in diamagnetism, paramagnetism and ferromagnetism in high magnetic fields. Ferromagnetism in weak magnetic fields—including the Barkhausen effect—is not so happily treated. This is no doubt because this part of the subject is still, as the author clearly states, almost without a theoretical structure to connect its phenomena. Aside from four misprints, a slight mistake regarding the magnetostriction of nickel-iron alloys on page 88, and a general tendency to use sub-visible subscripts, the reviewer finds nothing in which the author, editor, and publisher have been remiss. The practice of omitting the name of each investigator with whose conclusions the author disagrees is novel but commendable.

L. W. MCKEEHAN

Accoustics of Buildings. F. R. WATSON. Second Edition, Pp. 165, Figs. 69. John Wiley & Sons, New York, 1930. Price $3.00.

This is a second edition of Professor Watson's book first published in 1923, and is intended for that rapidly growing group of persons who have to deal with the practical problems of architectural acoustics. For this reason the emphasis throughout is laid upon the application of the developments in this field during the last thirty years to the control of acoustic conditions rather than upon a detailed account of the underlying principles and theory.

The first section of the book concerns itself with the problems of Auditorium Acoustics, particularly with the calculation and control of reverberation. Numerous illustrations and examples of the use of the reverberation formula both in the design of new rooms and in the correction of existing rooms are given. The most important addition made in the revision of this section of the book is a table of sound absorption coefficients of commercial materials used for acoustical correction, and one giving the absorbing power of opera chairs of various types. The author's position on the question of optimum reverberation times as a function of the size of the auditorium is somewhat equivocal. Thus a graph is given showing what the author considers the optimum time computed by the well-known Sabine formula increasing linearly with the logarithm of the volume from 0.8 to 2.05 seconds as the volume is increased from 1,000 to 1,000,000 cubic feet. In a subsequent paragraph under the heading "Ideal Auditorium Acoustics" appears the statement "The second condition (for ideal acoustics) is that the auditorium should be made as dead as out doors for the benefit of the auditors." The reader interested in the acoustical design of a new room is left in doubt as to whether to install absorbent material so as to give the "optimum reverberation time," or to try to approximate the "ideal" condition of out of doors where sound reflection is nil. The difference is one of considerable practical importance.

There are no important additions to the material given in the earlier edition in the section devoted to sound proofing in buildings, although numerous references to recent original work on this phase of the subject are added.

Considered even as a vehicle for the conveyance of practical information, one feels that the author frequently errs on the side of brevity and over simplification. This is particularly true in some of the illustrative diagrams. Thus to represent sound of wave-length of the order of two feet as being reflected in a parallel beam from a parabolic mirror with an aperture of five feet and reflected again geometrically from a plain surface of small dimensions is to neglect the complicated standing wave pattern that must result in such a case from interference and diffraction, and measurements based on such a simplified picture of the phenomenon must be open to serious question.

Taken as a whole the book is a concise, almost summary, statement of the principal facts of architectural acoustics as they were known at the time of the publication of the first edition of the book. To include the considerable mass of data that have been accumulated in the last five years would call for more rewriting than could be included in a revision of the first edition.

PAUL E. SABINE

Molekelbau. F. HUND. Pp. 38, 7 figs. and 3 tables. Part of Band VIII, Ergebnisse der exakten Naturwissenschaften, Julius Springer, Berlin, 1929.

This is a valuable compact summary of the progress made to date (i.e., spring of 1929) in the theory of molecular structure from the standpoint of the wave mechanics. The emphasis is laid on the qualitative features of the problem and no attempt is made to consider the mathematical arguments involved. The bibliography is comprehensive. The attention of persons interested in this review may also be called to the "Zusammenfassende Bericht" on homopolar chemical binding by W. Heitler in the Physikalische Zeitschrift for March, 1930, and to the articles on the "Interpretation of Band Spectra" by Mulliken now appearing in Reviews of Modern Physics.

E. C. KEMBLE